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## SOME ENERGY CHANGES CAUSED BY A RISE IN TEMPERATURE.*

BY J. E. MILLS.

If the ordinary ideas of matter, energy and motion are the correct ideas, all changes of energy must be due primarily to change either in the motion or position of matter. Hence when energy is added to or subtracted from a system consisting of similar molecules we may have energy changes due to change in the motion or position: first, of the system as a whole; second, of the molecules of the system; third, of the atoms composing the molecules and possibly the more elementary particles of which these atoms may consist. All of these possible energy changes are included in the following classification and it is adopted as affording a more convenient working basis.

I. A change in the motion or position of the system as a whole.

II. A change in the volume of the system, or more accurately a change in the relative position of the particles of the system each individual particle remaining as before. Here

* Thesis presented to the Faculty of the University of North Carolina for the degree of Doctor of Philosophy.

the changes may be conveniently subdivided as due to:

1. The external pressure.
2. The attraction of gravity.
3. Internal forces.

III. A change in the condition of the particles of the system. This head will include those energy changes due to changes in,

4. The translational motion of the molecule.
5. The possible rotational motion of the molecule, i. e., as a whole.
6. The forces of attraction or repulsion existing between the molecules, caused perhaps by the other changes mentioned.
7. The motion, kinetic energy, or position, potential energy, of the atoms within the molecule.

IV. Energy which may escape measurement, such as sound, light, heat, and electricity waves. To this source of error must be added the errors attendant upon all forms of measurement.

In the discussion to follow these energy changes will be designated $E_1$, $E_2$, etc., the subscript signifying to which case the energy change belongs. Also uniformly in this paper,

$M$ will represent the total mass of a body.
$m$ will represent the molecular mass.
$n$ will represent the number of molecules.
$p$ and $P$ will represent pressures.
$t$ ond $T$ will represent temperatures.
$v'$ and $V'$ will represent velocities.
$v$ and $V$ will represent volumes.
$d$ and $D$ will represent densities.
$\mu$ will denote absolute attraction or repulsion.
$\sigma_p$ denotes specific heat at constant pressure.
$\sigma_v$ denotes specific heat at constant volume.
$L$ = latent heat.
$\phi$ = coefficient of expansion under constant pressure.

## THE SPECIFIC HEAT OF A GAS.

Throughout this article the system as a whole will be

regarded as statical. Hence $E_I$ will always equal zero.

The amount of energy in calories necessary to raise one gram of a gas one degree without change of volume is represented by $\sigma_v$. Since the molecules of a gas can be assumed uniformly distributed throughout the space they occupy the relative position of the molecules must be unaltered. unless by reason of association or dissociation the number of molecules has changed. Hence $E_{II}$ is equal to zero and we will have $E_{III} = \sigma_v$ cals.

The specific heat at constant volume cannot be measured directly, save perhaps the experiments of Joly[1], but the ratio of the specific heat at constant pressure to the specific heat at constant volume can be measured, and calling this ratio $\gamma$ we have,

1. $\gamma = \frac{\sigma_p}{\sigma_v}$

2. $E_{III} = \sigma_v = \frac{\sigma_p}{\gamma}$

If the temperature of the gas be raised, the pressure remaining constant, a larger amount of energy is necessary equal to $\sigma_p$. Here $E_{II}$ is not zero and we have,

3. $E_{II} + E_{III} = \sigma_p$ cals., or $E_{II} = \sigma_p \frac{(\gamma - 1)}{\gamma}$, from 2.

$E_{II}$. It can be proved[2] that the amount of energy expended in overcoming a given constant external pressure will not be influenced by the shape assumed by the expanding body. Hence the energy expended will equal the pressure multiplied by the increment of volume and we have,

4. $E^1 = p\,(V - v)$ Ergs, where $p$ is the pressure in dynes and $v$ and $V$ the volume in cubic centimeters before and after expansion. Assuming the gas law to be obeyed we will have as usual,

5. $E_1 = R\,(T - t)$, where to calculate R we have, for the density of Hydrogen at 0° C. and 760 mm. pressure, at Lat.

45° and sea level, $d = .0000898765$[3]. The molecular weight of Hydrogen is taken as 2. The density of mercury is taken as 13.5956[4]. The value of gravity at Lat. 45° is 980.5966[5]. 0° C. is taken as 273° on the absolute scale. We use Rowland's value of the therm, as corrected by Day[6], $41.88 \times 10^6$ Ergs, assuming as the standard calorie the amount of energy necessary to raise one gram of water from 15° to 16° C. Thus we get,

$$6. \quad E_1 = \frac{1.9717}{m}(T - t) \text{ cals.}$$

For a more accurate calculation of $E_1$, which does not assume the gas laws to be obeyed, we multiply the volume by the coefficient of expansion of the gas under constant pressure $\phi$, and thus obtain the true increment of volume. So again we have,

$$7. \quad E_1 = \frac{p\phi}{D} = .024193\frac{\phi p}{D} \text{ cals., when } p \text{ is the pressure}$$

given in atmospheres, and $D$ is the density of the gas.

$E_2$. The work performed owing to the action of gravity upon the system depends upon the shape assumed by the expanding gas. For our purpose the effect is quite negligible since for one gram of gas in the most extreme case the energy change due to this cause would not exceed .0005 cal. per degree of expansion.

$E_3$. If forces of attraction or repulsion exist between the molecules it is evident that any change in the relative positions of the molecules will in general require or give out energy. The energy changes so caused are measured by $E_3$ and since $E_2$ is zero,

$$8. \quad E_3 = E_{II} - E_1 = \sigma_p - \frac{\sigma_p}{\gamma} - \frac{.024193\phi p}{D} \text{ from 3 and 7.}$$

Positive values of $E_3$ would correspond to an attraction, negative values to a repulsion, between the molecules. From

the data given below $E_3$ was calculated for seven gases and the result is shown for gram-molecular weights in Table 1, column 8, and per gram in column 9.

TABLE 1.

| 1 GAS | 2 Molecular Weight | 3 $\sigma_p$ | Authority | 4 $\gamma$ | Authority | 5 Coefficient of Expansion | Authority | 6 Density | Authority | 7 $E_1$ | 8 $E_3$ per gram molec'lar weight | 9 $E_3$ per gram |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | 2. | 3.4069 | 7 | 1.8966 | 14 | .0036613 | 21 | .0000898765 | 2 | 1.971 | —.0294 | —.0147 |
| CO | 27.78 | .24255 | 8 | 1.4000 | 15 | .0036688 | 22 | .0012514 | 29 | 1.970 | —.0140 | —.0005 |
| $N_2$ | 27.86 | .24390 | 9 | 1.4075 | 16 | .003673 | 23 | .0012501 | 30 | 1.980 | —.0127 | —.0004 |
| $O_2$ | 31.76 | .21751 | 10 | 1.4034 | 17 | .003674 | 24 | .0014290[illegible] | 31 | 1.975 | .0111 | —.0003 |
| $CO_2$ | 43.66 | .20122 | 11 | 1.2947 | 18 | .00371 | 25 | .0019771 | 32 | 1.982 | .0181 | .0004 |
| $N_2O$ | 43.74 | .22006 | 12 | 1.2938 | 19 | .0037195 | 26 | .0026870 | 33 | 1.886 | .3084 | .0070 |
| $SO_2$ | 63.59 | .15439 | 13 | 1.2554 | 20 | .004808 | 27 | .0039443 | 34 | 2.039 | —.2587 | —.0040 |
| | | | | | | .0039028 | | | | 2.251 | —.0417 | —.0006 |

It will be seen that $E_3$ thus calculated is so small as to be within the limits of experimental error and hence no dependence can be placed upon the result which is sometimes posi-

tive and sometimes negative. The failure to detect the molecular forces by this method is due perhaps, not so much to a lack of accuracy in the measurements. as to the fact that both the specific heat and the ratio of the specific heats alter slightly with the temperature and the measurements cited are not made at 0° but represent an average value over quite a range of temperature.

Yet another source of error which it has been found impossible to correct is due to the fact that specific heat is expressed in terms of the specific heat of water, and this latter value varies very considerably, and unfortunately the determinations of the amount of variation differ widely. It is only since the measurement of Rowland (1879), since confirmed by others[35a], that tolerably accurate values can be assigned the standard. In order to recalculate the specific heats of the gases to a uniform standard it would be necessary to know the temperatures of the calorimeter during the experiment, data which is not easily available.

In this connection it is well to remember that the experiments of Joule and Thomson[35] with the free expansion of gases showed a slight repulsion between the molecules of hydrogen and an attraction between the molecules of oxygen, nitrogen and carbon dioxide.

We may now safely assume that the error committed in making $E_3$ equal to zero will be negligible, and this gives us another method for calculating $\sigma_v$. For since $E_1 = E_{II}$, equation 3, becomes $E_3 = \sigma_p - \sigma_v$ or,

9. $\sigma_v = \sigma_p - E_3$.

Using gram-molecular weights the specific heat at constant volume calculated according to this equation is shown in column 5, Table 2. For $E_3$ the theoretical value given by equation 6 is used except for the seven gases shown in Table 1 where the true value as calculated from the observed density and coefficient of expansion was available. A comparison of these latter values with the theoretical will show an agreement quite close enough for our purpose. In column 6 the

specific heat at constant volume is shown calculated from the value $\sigma_v = \frac{\sigma_p}{\gamma}$. The difference between the two results is

TABLE 2.

| 1 GAS | 2 Molecular Weight | 3 $\sigma_p$ | Authority | 4 $\gamma$ | Authority | 5 $\sigma_v \times m$ from Eq. 9 | 6 $\sigma_v \times m$ from Eq. 2 | 7 5 − 6 | 8 $\sigma_p\left(\frac{\gamma-1}{\gamma}\right)m$ |
|---|---|---|---|---|---|---|---|---|---|
| 1. $H_2$ | 2. | 3.4069 | 7 | 1.3996 | 14 | 4.841 | 4.871 | −.030 | 1.942 |
| 2. $CH_4$ | 16.9 | .59295 | 37 | 1.3175 | 55 | 7.456 | 7.156 | .300 | 2.272 |
| 3. $NH_3$ | 16.93 | .52275 | 38 | 1.3028 | 56 | 6.879 | 6.793 | .086 | 2.057 |
| 4. $H_2O$ | 17.88 | .48051 | 39 | 1.3703 | 51 | 6.630 | 6.716 | −.096 | 1.875 |
| 5. CO | 27.78 | .24355 | 8 | 1.4090 | 15 | 4.768 | 4.782 | −.014 | 1.955 |
| 6. $N_2$ | 27.96 | .24380 | 9 | 1.4075 | 16 | 4.819 | 4.835 | −.013 | 1.966 |
| 7. NO | 29.81 | .23173 | 40 | 1.394 | 58 | 4.930 | 4.965 | −.019 | 1.962 |
| 8. $O_2$ | 31.76 | .21751 | 10 | 1.4084 | 17 | 4.933 | 4.922 | .0111 | 1.985 |
| 9. $H_2S$ | 33.89 | .24514 | 41 | 1.2918 | 59 | 6.321 | 6.432 | −.101 | 1.871 |
| 10. HCl | 36.18 | .19095 | 42 | 1.3947 | 60 | 4.915 | 4.939 | −.024 | 1.949 |
| 11. $CO_2$ | 43.66 | .20132 | 11 | 1.2947 | 18 | 6.803 | 6.785 | .018 | 1.999 |
| 12. $N_2O$ | 43.74 | .22095 | 12 | 1.2938 | 19 | 7.778 | 7.470 | .305 | 2.195 |
| 13. $C_2H_5OH$ | 45.68 | .45341 | 43 | 1.1365 | 61 | 18.740 | 18.224 | .516 | 2.487 |
| 14. $SO_2$ | 63.69 | .15439 | 13 | 1.2554 | 20 | 7.779 | 7.820 | −.042 | 1.997 |
| 15. $Cl_2$ | 70.96 | .1198 | 44 | 1.3295 | 62 | 6.457 | 6.340 | .117 | 2.089 |
| 16. $(C_2H_5)_2O$ | 73.48 | .4565 | 45 | 1.065 | 63 | 31.572 | 31.496 | .076 | 2.046 |
| 17. $CS_2$ | 75.56 | .15966 | 46 | 1.211 | 64 | 10.086 | 9.956 | .129 | 2.100 |
| 18. HBr | 80.34 | .0690 | 47 | 1.4089 | 65 | 4.616 | 4.676 | −.060 | 1.913 |
| 19. $C_2H_4Cl_2$ [48a] | 98.16 | .22081 | 48 | 1.1113 | 66 | 20.597 | 20.355 | .282 | 2.251 |
| 20. $CHCl_3$ | 118.44 | .1465 | 49 | 1.122 | 67 | 15.380 | 15.465 | −.085 | 1.886 |
| 21. HI | 126.89 | .0550 | 50 | 1.397 | 68 | 5.007 | 4.996 | .021 | 1.983 |
| 22. $Br_2$ | 158.68 | .05541 | 51 | 1.298 | 69 | 6.821 | 6.800 | .021 | 1.992 |
| 23. ClI | 161.07 | .0512 | 52 | 1.318 | 70 | 6.275 | 6.257 | .018 | 1.989 |
| 24. $SiCl_4$ | 168.92 | .1322 | 53 | 1.129 | 71 | 20.360 | 19.779 | .580 | 2.550 |
| 25. $I_2$ | 251.78 | .0396 | 54 | 1.394 | 72 | 6.488 | 6.537 | −.049 | 1.923 |

shown in column 7. The two calculated values of the specific heat show the best agreement with those gases which have been the subject of the most accurate measurement and it is

[2]

probable therefore that any lack of agreement indicates either an inaccuracy in the measurements given, or that, owing to association or dissociation of molecules, the molecular weight given is not correct.

By substituting for $\sigma_v$ in equation 9 its value $\frac{\sigma_p}{\gamma}$ and multiplying through by $m$ we have, after transposing,

10. $E_1 \times m' = \sigma_p \left( \frac{\gamma - 1}{\gamma} \right) m = 1.9717$, for a difference of one degree, from equation 6.

Since a function of the three measurements here equals a constant this equation affords us an excellent means of comparing the measurements with the theory. The result of the comparison is shown in column 8, Table 2. Of the twenty-five gases for which measurements were obtained seventeen are within five per cent. of the theoretical. The greatest error is in the case of $SiCl_4$, nearly thirty per cent, and for four others, $CH_4$, $N_2O$, $C_2H_5OH$, and $C_2H_4Cl_2$, ethylene chloride, the error is more than ten per cent.

It is evident that equation 10 gives us a method of determining the molecular weight of a gas by a measurement of its specific heat at constant pressure and the ratio of its specific heats.

$E_4$. If a molecule of mass $m$ is moving with velocity $V'$ then we have for the kinetic translational energy of the molecule,

11. $E_4 = \frac{1}{2} m V'^2$.

Now from the kinetic theory of gases, on the supposition that each molecule has the same average velocity $V'$, we have when $M$ is the mass of the gas in volume $V$,

12. $PV = \frac{MV'^2}{3} = RT.$

The supposition made is not strictly accurate for Maxwell

has shown[18] that some of the molecules have a velocity much greater, others much smaller, than the average. Hence instead of the mean velocity squared, which we use by definition, viz.: $\omega = \left(\frac{V'_1 + V'_2 + \text{- - - } V'_n}{n}\right)^2$, we really use $\frac{V'^2_1 + V'^2_2 + \text{- - - } + V'^2_n}{n}$, where $n$ is the number of molecules and $V'$ with subscripts the actual velocity of each molecule. But the error thus introduced as was further shown by Maxwell, amounts to but little, for only a very few of the molecules differ greatly from the average in velocity. The relation between the two values is given by the equation[73a]

$$13. \quad \omega = \left(\frac{8}{3\pi}\right)^{\frac{1}{2}} V' = .9213\ V'.$$

From equation 12 we have $T = \frac{MV'^2}{3R}$ and combining with 11 we get,

$$14. \quad E_t = \frac{3RT}{2} = 2.9576 \frac{T}{m} = \frac{2.9576}{m} \text{ when } T = 1°.$$

This equation is evidently a straight line and can be at once drawn to scale for any particular gas, its molecular weight being known. Also at corresponding temperatures gram-molecular weights of all gases represent the same amount of kinetic translational energy.

Equation 14 has been long thought to be true for gases. Now, however, we have the very same reasons for believing that temperature is a measure of the kinetic translational energy of the molecules of a liquid, for, first, the molecules of a liquid are free to move among each other, having no definite position and hence on the principle established by Maxwell[74] the average energy of the molecules must in time become the same. Second, it has been shown by Van't Hoff[75]

that the osmotic pressure of a dissolved molecule in a solution was the same as the pressure of a gas molecule under the same conditions of concentration and temperature, and the gas law $PV = RT$ holds true for solutions. If the dissolved substance dissociates the number of molecules in the solution must be increased $\left(\frac{PV}{i} = RT$, $i$ being the Van't Hoff coefficient$\right)$ but the principle underlying the law remains unchanged—a dissolved molecule exerts the same pressure as would a gaseous molecule under similar conditions.

Since a gaseous molecule exerts pressure because of its translational energy, it seems a necessary conclusion that if a dissolved molecule exerts an equal pressure its translational energy must be the same. Mechanically it is quite impossible that the dissolved molecule should have and maintain a different average amount of translational energy than is possessed by the molecules of the solvent. So we reach a conclusion, which has been expressed by others[76], that the average translational energy of gaseous and liquid molecules must at the same temperature be equal.

Since it is not admitted that the molecules of a solid are in free motion, Maxwell's conclusions are not as inevitable for solids as for gases, and other evidence is not yet sufficient to justify the application of equation 14 to solids.

Since $E_t$ varies inversely as the molecular weight, for a rise in temperature of one degree more energy will be required for the kinetic translational motion as dissociation proceeds. Were it not that less energy per molecule seems then to be required for internal work this would give us a measure of the amount of dissociation.

Again we have from equations 12 and 13 if $M = 1$,

15. $V' = 1.0854\,\omega = (3\,RT)^{\frac{1}{2}} = 15740\left(\frac{T}{m}\right)^{\frac{1}{2}}$ cms. per second. Hence the curve connecting the velocity of a molecule and its temperature is a parabola.

Dulong and Petit showed that the specific heat of the elements, as solids, multiplied by their atomic weight equalled a constant, very approximately, though a few elements, as beryllium, carbon and silica gave widely divergent values when the specific heat was determined at the ordinary temperature. The expansion of solids being very slight the amount of energy spent in overcoming external pressure is inappreciable. The attractive force between the molecule is very much greater in solids than in gases, owing to the fact that the molecules are very much closer together. Yet for variations of 1° C the expansion of the solid is so little that probably only a very small amount of energy is spent in overcoming the attraction as the molecules shift their position. This idea is supported by the fact that the specific heat of water between 0° and 4° C. continues to increase while its volume diminishes. The conclusion we would draw is, that energy spent in shifting the position of the molecules is of minor importance and that practically the entire specific heat of the solid is spent upon the molecule, or upon the atoms within the molecule.

From this it will be seen that the specific heat of the solid corresponds to the specific heat at constant volume of the gas and if this latter be multiplied by the molecular weight of the gas we will obtain a quantity analagous to the constant of Dulong and Petit. The results have already been given in columns 5 and 6, of Table 2. No regularity is at first apparent.

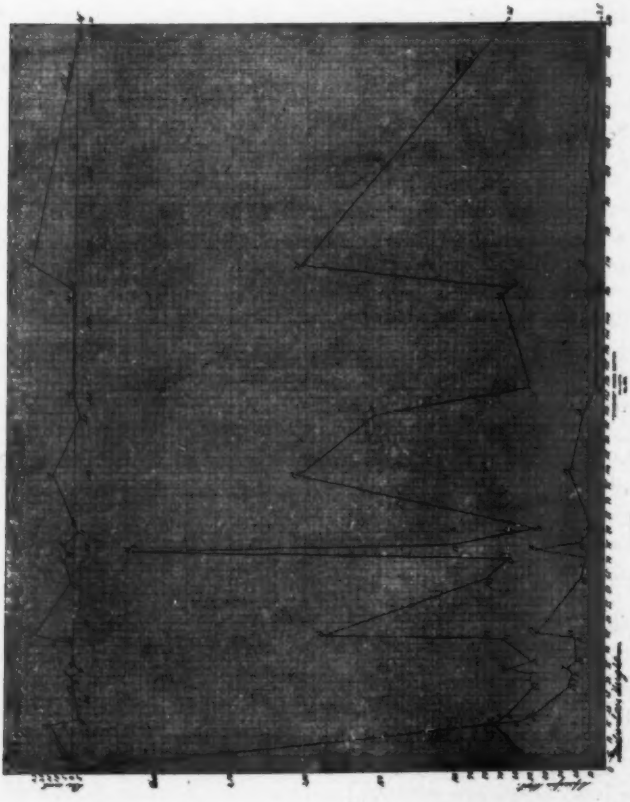
Since we are trying to find a relation between the molecular weight of the gases and their specific heat, in Diagram 1, the molecular weights of the twenty-five gases given in Table 2 are plotted as abscissa. The specific heats are then plotted on an arbitrary scale as ordinates, and the points thus given (denoted by number corresponding to the gases, see Table 2) are joined and constitute curve 1. Of course the gases chosen are without relation to each other and the points are entirely distinct. They are joined merely to present a connected and more easily comprehended whole.

It will be seen that the specific heat is greatest when the

molecular weight is least and decreases with marked irregularities as the molecular weights increase.

In a similar manner and with a different arbitrary unit line

DIAGRAM 1.



2 represents the product of the molecular weight and the specific heat at constant volume given in column 5, Table 2. Had the specific heat as calculated in column 6 been used the

line would follow line 2 so closely as to be usually indistinguishable on the scale adopted.

Since $E_i \times m$ = constant and $\sigma_p - E_i = \sigma_v$, line 2 represents the $\sigma_p \times m$ equally as well as it does the $\sigma_v \times m$, the one line differing from the other by a constant and the unit chosen being arbitrary.

A study of line 2 shows instead of a regularity analagous to the law of Dulong and Petit, an irregularity most marked. A theory first given by J. J. Waterston to the Royal Society in 1845 and later rediscovered by Clausius[76a] can be used to throw light upon this subject. If the total internal energy of a molecule as distinguished from the kinetic translational motion of the molecule be denoted by $E_i$ then the specific heat at constant volume $= E_t + E_i$ and the specific heat at constant pressure $= E_i + E_t + E_i$. Since for a rise in temperature of 1° C., $E_t = \frac{3}{2}R$ and $E_i = R$ we have,

$$16.\quad \gamma = \frac{\sigma_p}{\sigma_v} = \frac{R + \frac{3}{2}R + E_i}{\frac{3}{2}R + E_i} = \frac{5R + 2E_i}{3R + 2E_i}.$$

This is the theory as given by Waterston. Now if we throw the equation into the form,

$$17.\quad \gamma = \frac{\frac{5}{3}E_t + E_i}{E_t + E_i}$$ by putting for R its value $\frac{2}{3}E_t$, we have

here a relation which gives the value of $\gamma$ in terms of the kinetic translational motion of the molecule and the internal energy.

The relation $\gamma = \frac{\sigma_p}{\sigma_v}$ has no meaning if applied to liquids or solids, while the relation $\gamma = \frac{\frac{5}{3}E_t + E_i}{E_t + E_i}$, *has a meaning as clear and definite when applied to solid and liquid bodies as to gaseous.*

This meaning throws a new light on the results given in

Table 2, column 8. These results are shown diagrammatically by line 3, diagram 1, the scale being so chosen that each division from the central line means a departure of one per cent from the theoretical. There the relation theoretically deduced $\sigma_p\left(\frac{\gamma-1}{\gamma}\right)m =$ constant, was tested and found to give very approximately a constant, seventeen out of the twenty-five gases being within five per cent. of the theoretical.

Now if we put $\frac{\sigma_p}{\gamma} = \sigma_v$ we have,

18. $\sigma_v(\gamma - 1)\, m =$ constant.

*In this latter form the equation should hold alike for molecules of solid, liquid and gas, since we have seen that both $\sigma_v$ and $\gamma$ applied to molecules of liquids and solids have a meaning capable of a physical interpretation.*

Since the law of Dulong and Petit is $\sigma_v \times m =$ constant and the equation deduced gives $\sigma_v \times m\,(\gamma - 1) =$ constant, it will be seen that the latter equation adds another factor to the law of Dulong and Petit. Now as will be subsequently shown, though it is a fact already known, $\gamma$ for gases, and consequently we would argue $\gamma$ for liquids and solids also, is determined principally by the number of atoms of which the system is composed and it is to a less extent dependent upon the way in which the atoms are put together. That is, $\gamma$ is approximately a constant for all the gases having the same number of atoms in the molecule, and is still nearer a constant if these gases are chemically similar.

From which it follows that for those elements which have the same number of atoms in the molecule, equation $\sigma_v \times m\,(\gamma - 1) = c$, will become identical with the law of Dulong and Petit, since $\gamma$ will for them be a constant. When however the number of atoms in the molecule increases $\gamma$ changes, diminishing as will be seen, and for these cases the equation cited above will give a smaller value than required

by the law of Dulong and Petit, provided the old molecular weight be used. This would correspond to the case of carbon, silicon, boron, etc., which present exceptions to the law of Dulong and Petit.

It may be further pointed out here that Neumann in 1831 showed a law similar to the law of Dulong and Petit to exist for solid compounds of similar chemical character. That is the product of their specific heat and molecular weight equalled a constant, though a different constant for each dissimilar series. This is exactly what the equation derived above would lead us to expect, since $\gamma$ would remain constant for bodies of similar chemical constitution but would change when the structure of the molecule changed.

Again we have the total internal energy of the molecule $E_i = E_5 + E_6 + E_7 = E_{III} - E_4 = \sigma_v - E_4$.

For a rise in temperature of one degree we can put for $\sigma_v$ its value $= \sigma_p - E_s = \sigma_p - \frac{R_c}{m}$, when $R_c = mR$ and for $E_4$ its value $= \frac{1}{2}\frac{R_c}{m}$, whence we get,

19. $E_i = \sigma_p - \frac{1}{2}\frac{R_c}{m}$. If however we put for $\sigma_v$ its value $\frac{\sigma_p}{\gamma} = \frac{E_i + \frac{1}{2}\frac{R_c}{m}}{\gamma}$ we get,

20. $E_i = \frac{R_c}{2m} \times \frac{5 - 3\gamma}{\gamma - 1}$. From this equation it will seen that $E_i = 0$ when $\gamma = \frac{5}{3}$ and $E_i = \infty$ when $\gamma = 1$. The two equations 19 and 20 of course become identical when the relation given by equation 10, viz., $\sigma_p \frac{\gamma - 1}{\gamma} = \frac{R_c}{m}$ holds.

TABLE 3.

| 1 SUBSTANCE | 2 Molecular Weight | 3 Specific Heat at Constant Pressure | Authority | 4 Ratio of Specific Heats | Authority | 5 $\sigma_v \times m$ from Equa'on 9 | 6 $\sigma_p \times m$ from Equa'on 2 | 7 $E_i$ from Equa'on 19 | 8 $E_i$ from Equa'on 20 | 9 $E_i \div$ Number of Atoms | 10 $\frac{E_i}{E_4}$ | 11 $\sigma_v \div$ Number of Atoms |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Hydrogen, $H_2$ | 2. | 3.4062 | 7 | 1.3986 | 14 | 4.841 | | 1.883 | | .942 | .636 | 2.421 |
| 2. Helium, He | 3.96 | | | 1.6666 | 77 | | 2.958 | | | | | 2.958 |
| 3. Methane, $CH_4$ | 15.9 | .59295 | 37 | 1.3175 | 55 | 7.456 | 6.210 | 4.499 | 3.25 | .900 | 1.52 | 1.491 |
| 4. Ammonia, $NH_3$ | 16.93 | .52275 | 38 | 1.3028 | 56 | 6.879 | | 3.921 | | .980 | 1.32 | 1.720 |
| 5. Water, $H_2O$ | 17.88 | .48051 | 39 | 1.2793 | 57 | 6.620 | | 3.662 | | 1.221 | 1.240 | 2.207 |
| 6. Acetylene, $C_2H_2$ | 25.8 | | | 1.26 | 78 | | 7.582 | | 4.62 | 1.156 | 1.564 | 1.895 |
| 7. Carbon monoxide, CO | 27.78 | .24255 | 8 | 1.409 | 15 | 4.768 | | 1.810 | | .905 | .611 | 2.384 |
| 8. Ethylene, $C_2H_4$ | 27.80 | .4071 | 79 | 1.2496 | 80 | | 7.900 | | 4.94 | .824 | 1.671 | 1.317 |
| 9. Nitrogen, $N_2$ | 27.86 | .2438 | 9 | 1.4075 | 16 | 4.812 | | 1.854 | | .927 | .626 | 2.406 |
| 10. Nitric oxide, NO | 29.81 | .23173 | 40 | 1.394 | 58 | 4.936 | | 1.979 | | .989 | .669 | 2.468 |
| 11. Oxygen, $O_2$ | 31.76 | .21751 | 10 | 1.4034 | 17 | 4.933 | | 1.975 | | .987 | .667 | 2.467 |
| 12. Methyl alcohol, $CH_3OH$ | 31.78 | .45802 | 81 | | | 12.584 | | 9.627 | | 1.604 | 3.25 | 2.097 |
| 13. Hydrogen sulphide, $H_2S$ | 33.83 | .24514 | 41 | 1.2913 | 59 | 6.321 | 6.762 | 3.363 | 3.80 | 1.121 | 1.135 | 2.107 |
| 14. Hydrochloric acid, HCl | 36.18 | .19035 | 42 | 1.3947 | 60 | 4.915 | | 1.957 | | .978 | .661 | 2.458 |
| 15. Argon, A | 39.92 | | | 1.653 | 82 | | 2.958 | | | | | 2.958 |
| 16. Carbon dioxide, $CO_2$ | 43.66 | .20122 | 11 | 1.2947 | 18 | 6.803 | | 3.845 | | 1.282 | 1.30 | 2.268 |
| 17. Methyl aldehyde, $C_2H_4O$ | 43.68 | | | 1.1455 | 83 | | 13.547 | | 10.59 | 1.513 | 3.582 | 1.935 |
| 18. Nitrous oxide, $N_2O$ | 43.74 | .22095 | 12 | 1.2938 | 19 | 7.778 | 6.713 | 4.820 | 3.75 | 1.607 | 1.63 | 2.593 |
| 19. Alcohol, $C_2H_5OH$ | 45.68 | .45341 | 43 | 1.1365 | 61 | 18.740 | 14.448 | 15.783 | 11.49 | 1.754 | 5.33 | 2.082 |
| 20. Methyl ether, $(CH_3)_2O$ | 45.68 | | | 1.110 | 84 | | 17.918 | | 14.96 | 1.662 | 5.06 | 1.991 |
| 21. Chlor methane, $CH_3Cl$ | 50.08 | | | 1.1991 | 85 | | 9.888 | | 6.93 | 1.386 | 2.347 | 1.975 |
| 22. Ethyl cyanide, $C_2H_5CN$ | 54.63 | .42616 | 86 | | | 21.309 | | 18.352 | | 2.039 | 6.20 | 2.368 |
| 23. Acetone, $C_3H_6O$ | 57.58 | .37775 | 87 | | | 19.779 | | 16.821 | | 1.682 | 5.68 | 1.978 |
| 24. Sulphur dioxide, $SO_2$ | 63.59 | .15439 | 13 | 1.2554 | 20 | 7.779 | | 4.821 | | 1.607 | 1.63 | 2.593 |
| 25. Ethyl chloride, $C_2H_5Cl$ | 63.98 | .27877 | 110 | 1.1257 | 88 | | 15.668 | | 12.71 | 1.589 | 4.30 | 1.958 |
| 26. Chlorine, $Cl_2$ | 70.36 | .1198 | 44 | 1.3295 | 62 | 6.457 | 5.988 | 3.499 | 3.03 | 1.749 | 1.180 | 3.228 |
| 27. Ethyl formate, $C_3H_6O_2$ | 73.46 | | | 1.124 | 89 | | 15.898 | | 12.94 | 1.176 | 4.377 | 1.445 |
| 28. Methyl acetate, $C_3H_6O_2$ | 73.46 | | | 1.137 | 90 | | 14.398 | | 11.44 | 1.040 | 3.867 | 1.309 |
| 29. Ethyl ether, $(C_2H_5)_2O$ | 73.48 | .4565 | 45 | 1.065 | 63 | 31.572 | | 28.614 | | 1.908 | 9.670 | 2.105 |

TABLE 3.—CONTINUED.

| SUBSTANCE | 2 Molecular Weight | 3 Specific Heat at Constant Pressure | Authority | 4 Ratio of Specific Heats | Authority | 5 $\sigma_v \times m$ from Equa'on 9 | 6 $\sigma_p \times m$ from Equa'on 2 | 7 $E_t$ from Equa'on 19 | 8 $E_t$ from Equa'on 20 | 9 $E_t \div$ Number of Atoms | 19 $\frac{E_t}{E_4}$ | 11 $\sigma_v \div$ Number of Atoms |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30. Methylal, $C_3H_8O_2$ | 75.46 | | | 1.078 | 91 | | 25.278 | | 22.32 | 1.717 | 7.547 | 1.944 |
| 31. Carbon disulphide, $CS_2$ | 75.56 | .15956 | 46 | 1.211 | 64 | 10.085 | 9.348 | 7.127 | 6.39 | 2.376 | 2.405 | 3.362 |
| 32. Allyl chloride, $C_3H_5Cl$ | 75.88 | | | 1.137 | 92 | | 14.398 | | 11.44 | 1.271 | 3.866 | 1.599 |
| 33. Benzene, $C_6H_6$ | 77.4 | .33563 | 93 | | | 23.969 | | 21.011 | | 1.751 | 7.100 | 1.997 |
| 34. Hydrobromic acid, HBr | 80.34 | .0820 | 47 | 1.4089 | 65 | 4.616 | | 1.659 | | .829 | .560 | 2.308 |
| 35. Dichlor methane, $CH_2Cl_2$ | 84.26 | | | 1.169 | 94 | | 11.66 | | 8.70 | 1.740 | 2.943 | 2.332 |
| 36. Ethyl acetate, $C_4H_8O_2$ | 87.36 | .3697 | 95 | | | 30.325 | | 27.368 | | 1.955 | 9.240 | 2.166 |
| 37. Ethyl mercapatan, $(C_2H_5)_2S$ | 89.43 | .40081 | 96 | | | 33.873 | | 30.915 | | 2.061 | 10.450 | 2.258 |
| 38. Ethylene chloride, $C_2H_4Cl_2$ | 98.16 | .22931 | 48 | 1.1112 | 66 | 20.537 | 17.74 | 17.580 | 14.78 | 2.197 | 5.940 | 2.567 |
| 39. Ethylidene chloride, $C_2H_4Cl_2$ | 98.16 | | | 1.134 | 97 | | 14.71 | | 11.75 | 1.469 | 3.973 | 1.840 |
| 40. Vingl bromide, $C_2H_3Br$ | 106.14 | | | 1.198 | 98 | | 9.96 | | 7.00 | 1.167 | 2.366 | 1.660 |
| 41. Ethyl bromide, $C_2H_5Br$ | 108.14 | .17503 | 76b | | | 16.956 | | 13.998 | | 1.750 | 4.730 | 2.119 |
| 42. Chloroform, $CHCl_3$ | 118.44 | .1465 | 49 | 1.122 | 67 | 15.380 | | 12.422 | | 2.484 | 4.195 | 3.076 |
| 43. Allyl bromide, $C_3H_5Br$ | 120.04 | | | 1.145 | 99 | | 13.60 | | 10.64 | 1.182 | 3.597 | 1.511 |
| 44. Phosphorous, $P_4$ | 123.00 | | | 1.175 | 100 | | 11.27 | | 8.31 | 2.078 | 2.810 | 2.817 |
| 45. Hydriodic acid, HI | 126.89 | .0550 | 50 | 1.397 | 68 | 5.007 | | 2.050 | | 1.025 | .692 | 2.504 |
| 46. Ethane trichloride, $C_2H_3Cl_3$ | 132.34 | | | 1.0871 | 101 | | 53.14 | | 50.18 | 6.272 | 16.966 | 6.642 |
| 47. Turpentine, $C_{10}H_{16}$ | 135.00 | .5061 | 102 | | | 66.352 | | 63.394 | | 2.438 | 21.400 | 2.552 |
| 48. Phosphorous trichloride, $PCl_3$ | 136.29 | .13473 | 103 | | | 16.391 | | 13.433 | | 3.358 | 4.540 | 4.098 |
| 49. Carbon tetrachloride, $CCl_4$ | 152.62 | | | 1.130 | 104 | | 15.16 | | 12.20 | 2.44 | 4.127 | 3.034 |
| 50. Bromine, $Br_2$ | 158.68 | .05541 | 51 | 1.293 | 69 | 6.821 | | 3.861 | | 1.932 | 1.305 | 3.410 |
| 51. Chlor iodide, Cl I | 161.07 | .0512 | 52 | 1.318 | 70 | 6.275 | | 3.317 | | 1.659 | 1.12 | 3.138 |
| 52. Silicon tetrachloride, $SiCl_4$ | 168.92 | .1322 | 53 | 1.129 | 71 | 20.360 | 15.28 | 17.402 | 12.32 | 3.480 | 5.88 | 4.072 |
| 53. Arsenic trichloride, $AsCl_3$ | 179.99 | .11224 | 105 | | | 18.230 | | 15.273 | | 3.818 | 5.16 | 4.558 |
| 54. Titanium tetrachloride, $TiCl_4$ | 188.52 | .12897 | 106 | | | 22.342 | | 19.384 | | 3.877 | 6.55 | 4.468 |
| 55. Mercury, Hg | 198.50 | | | 1.667 | 107 | | 2.958 | | | | | 2.958 |
| 56. Brom-iodide, BrI | 205.23 | | | 1.33 | 108 | | 5.98 | | 3.02 | 1.510 | 1.02 | 2.990 |
| 57. Iodine, $I_2$ | 251.78 | .0336 | 54 | 1.294 | 72 | 6.488 | | 3.530 | | 1.765 | 1.195 | 3.244 |
| 58. Tin tetrachloride, $SnCl_4$ | 258.82 | .09388 | 109 | | | 22.326 | | 19.369 | | 3.874 | 6.545 | 4.465 |

Using these equations we are enabled to calculate the total internal energy of a molecule directly from a measurement either of the specific heat of the gas at constant pressure or from the ratio of the specific heats. This we have done for gram-molecular weights of the fifty-eight gases shown in Table 3. Column 7 contains $E_i$ calculated from $\sigma_p$ according to equation 19 except for the seven gases shown in Table 1 where the observed value for $E_i$ was substituted for the calculated value. Column 8 contains the calculated value of $E_i$ from $\gamma$ according to equation 20. As has been pointed out the equations are identical when the relation shown in equation 10 holds. For the eight gases, $CH_4$, $H_2S$, $N_2O$, $C_2H_5OH$, $Cl_2$, $CS_2$, $C_2H_4Cl_2$, $SiCl_4$, where this relation varies over five per cent from the theoretical, $E_i$ was calculated both from $\gamma$ and from $\sigma_p$. When the agreement was more exact it was regarded as useless to duplicate the calculation.

Again plotting the molecular weights as abscissa, and $E_i$ as ordinates, on an arbitrary scale we show the results of columns 7 and 8 diagrammatically in Diagram 2, line 1. As before the points are joined only to present to the eye a connected whole. It is quite evident that $E_i$ is not a function of the *molecular* weight.

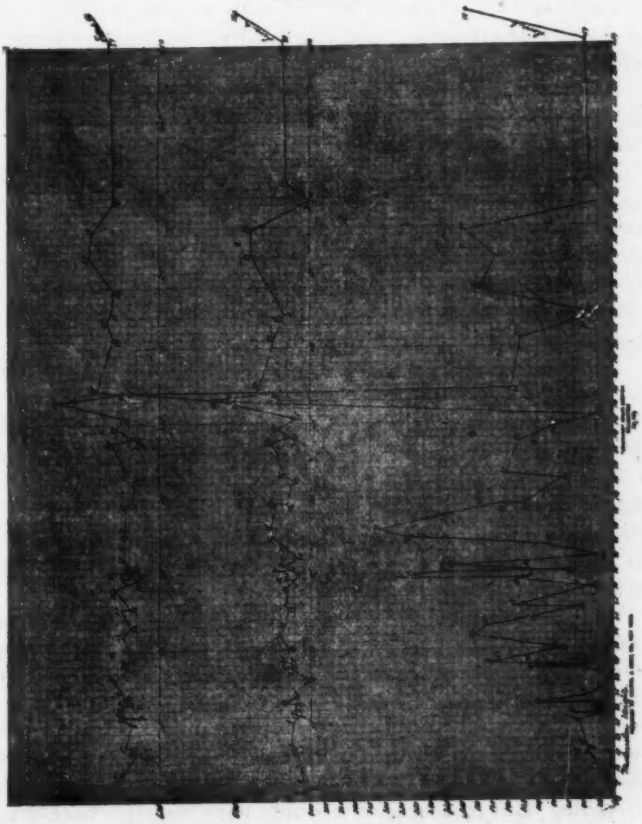
Since $E_i \times m$ differs from $\sigma_v \times m$ only by a constant, the line can be taken equally well as representing these values and can thus be regarded as an extension of the line 2 shown in Diagram 1.

$E_6$. We have already concluded from Table 1 that the forces of attraction or repulsion existing between the molecules of a gas is an inappreciably small quantity. The changes in attraction represented by $E_6$ must necessarily be infinitesimals of a yet higher order. In dealing with gases then, through slight changes in temperature, we may safely put $E_6 = 0$ within the limit of experimental error.

This leaves the internal energy of the molecule $E_i = E_5 + E_7$. The attempt of the kinetic theory of gases is to explain the phenomena of gases from known mechanical principles assum-

ing that the laws which govern masses of matter are applicable to molecules and atoms as well. The efforts on this line to explain the true office of the "internal" energy of a gas

DIAGRAM 2.



have not been satisfactory as to results. So little is known of the actual framework of the molecule that it is impossible to approach the problem in a direct manner. The various

reductio ad absurdum sort of arguments which have been developed to point to the most probable conclusion seem to require a more minute discussion of one or two possibilities.

*Consider the molecule as a rigid body capable of rotation.*

This supposition cannot be put aside as inherently too improbable to warrant investigation. For the force, chemical affinity, which holds the atoms together is often much greater (say fifty times) than the force of cohesion which binds the particles of a solid. It might be possible then that the molecules, even under the stress of a collision, behave as nearly rigid bodies. And this possibility is further justified by the fact that monatomic gases (as shown by mercury, also argon and helium, though in these latter cases the fact that they are monatomic is established by this argument) show no evidence of internal heat energy, i.e. *behave mechanically as rigid spheres.* Many chemists at heart believe in the complexity of even a monatomic molecule.

We know that if the temperature be sufficiently raised most molecular structures break down and this decomposition is usually a gradual process. Certain it is that energy is required to produce this disseggregation in all exothermic bodies and the energy is not supplied all at once but gradually and must constitute a part of the specific heat of the body. It might however be supplied by increasing the centrifugal force, i.e. the tendency to fly apart, of the molecules. Whether or not *all* of it is so supplicd we have a means of judging.

For if we consider all of the factors which produce the rotation (page 25) it will be seen that they all must remain constant with increase of temperature except the average energy of the colliding body. This would necessitate that $E_s$, which is equal to $E_i$ (if the system be rigid) should be strictly proportional to the temperature and since $E_s$ is also proportional to the temperature, $\sigma_v$, which is equal to their sum must be invariable. But measurements which have thus far been made and which are shown in Table 4, prove that it is within only rather narrow limits that the $\sigma_p$ and hence the $\sigma_v$, can be con-

TABLE 4.

| 1 SUBSTANCE | 2 Temperature | 3 $\sigma_p$ | Authority | 4 SUBSTANCE | 5 Temperature | 6 $\gamma$ | Authority |
|---|---|---|---|---|---|---|---|
| Air | —30°, 10° | .23771 | 129 | Air | 0° | 1.40526 | 117 |
| | 0, 100 | .32741 | | | 100 | 1.40289 | |
| | 0, 200 | .23751 | | | | | |
| CO | 23, 99 | .2425 | 133 | CO | 0 | 1.40320 | 122 |
| | 26, 198 | .2426 | | | 100 | 1.39465 | |
| $CO_2$ | —28, 7 | .18427 | 134 | $CO_2$ | 0 | 1.31131 | 123 |
| | 15, 100 | .20246 | | | 100 | 1.28212 | |
| | 11, 214 | .21692 | | | | | |
| $N_2O$ | 26, 103 | .2126 | 135 | $N_2O$ | 0 | 1.3106 | 124 |
| | 27, 206 | .2241 | | | 100 | 1.27238 | |
| $NH_3$ | 33, 100 | .5202 | 136 | $NH_3$ | 0 | 1.3172 | 125 |
| | 27, 200 | .5356 | | | 100 | 1.2770 | |
| $C_2H_4$ (Impure) | 24, 100 | .3880 | 137 | $C_2H_4$ | 0 | 1.24548 | 126 |
| | 27, 200 | .4293 | | | 100 | 1.1870 | |
| $NO_2$ | 27, 67 | 1.625 | 141 | $N_2O_4$, 15 per cent dissociated | 20 | 1.172 | 142 |
| | 27, 150 | 1.115 | | 57 " " | 22 | 1.274 | |
| | 27, 280 | .65 | | 100 " " | 150 | 1.31 | |
| $(C_2H_5)_2O$ | 25, 111 | .4280 | 130 | $C_3H_8O_2$ (Methylal) | 12.7 | 1.0650 | 127 |
| | 27, 189 | .4618 | | | 22.5 | 1.0750 | |
| $C_6H_6$ | 34, 115 | .2990 | 131 | | 31, 42 | 1.0940 | |
| | 35, 180 | .3325 | | $(CH_3)_2O$ | 5.7 | 1.1072 | 128 |
| $C_4H_8O_2$ (Ethyl acetate) | 35, 189 | .3374 | 132 | | 30.3 | 1.1127 | |
| | | .3709 | | ClI | 100 | 1.315 | 118 |
| $H_2$ | —28, 9 | 3.3996 | 138 | | 200 | 1.321 | |
| | 12, 198 | 3.4090 | | HCl | 20 | 1.389 | 119 |
| $C_3H_6O$ (Acetone) | 26, 110 | .3468 | 139 | | 100 | 1.400 | |
| | 27, 179 | .3740 | | HBr | 20 | 1.422 | 120 |
| $CHCl_3$ | 27, 118 | .1441 | 140 | | 100 | 1.440 | |
| | 28, 189 | .1489 | | HI | 20 | 1.397 | 121 |
| | | | | | 100 | 1.396 | |

sidered to be constant. Hence it is only between these limits that we can conceive of the molecule as even approximately rigid.

Column 3, Table 4, shows the variations of the specific heat at constant pressure for the temperatures recorded in Column 2. Also column 6 shows the variations in $\gamma$ for the temperatures recorded in column 5.

It will be seen,

*a.* That the change in the value of $\sigma_p$ and $\gamma$ is of opposite sign. This is what would be true if the energy change were taking place inside the molecule.

*b.* For the diatomic gases the change in the specific heat is very slight or nil, but the change becomes more apparent with increasing complexity of the molecule. This would again point to constitutional changes within the molecule.

*c.* When $N_2O_4$ dissociates into $NO_2$, the change both in $\sigma_p$ and $\gamma$ is very decided and rapid, adding further evidence to the belief that a change in the specific heat denotes a change in constitution.

*d.* The specific heat, as also $\gamma$, sometimes increases and sometimes decreases with the temperature. This finds a simple explanation in the fact that addition of energy causes not only progressive constitutional changes but at a certain point, a change in the molecular weight and the number of molecules as well. Thereby $E_1$ and $E_4$ are changed.

*e.* The specific heat increases with the density of the gas according to the determinations of Lussana[145] for a series of gases. Joly[143] found for hydrogen a similar increase and for carbon dioxide at 7.2 atmospheres the specific heat at constant volume .16841 and at 21.66 atmospheres .17386. For air at 19.5 atmospheres he obtained the specific heat at constant volume .1721, a similar increase. On the other hand Regnault[144] could detect no variation in the specific heat of hydrogen, one to nine atmospheres, and air, one to twelve atmospheres. Since the specific heat of a substance as a liquid is always greater than than the specific heat of the substance

as a gas it would seem that the specific heat of the gas must increase with the density and the facts cited above warrant the conclusion.

Although the variations in $\sigma_p$ and $\gamma$ shown above are too marked to admit of a belief in the rigidity of a molecule over wide ranges of temperature, they do not preclude the idea that molecules may behave as nearly rigid bodies up to a certain temperature. (Only a rigidity relative to the centroid of the molecule is here meant. The atoms may vibrate, or the molecule as a whole.) Hence it is necessary to pursue our original supposition further.

In a nearly rigid system the actual amount of energy expended by a collision will depend: *a*. On the rotational motion of the systems. *b*. On the velocity of the centers of gravity and the masses of the systems. *d*. On the point of application of the impact. *e*. On the elasticity and rigidity of the systems.

In the discussion which follows it should be borne in mind that we are not trying to get the average amount of rotational energy produced (added) by a collision for this is of course zero. But we do wish to find the amount of rotational energy produced by a single impact upon another molecule assumed at rest. And the aforesaid single impact must represent exactly the average impact upon the molecule. Considering *a*, all systems can be represented by particles revolving around their centre of gravity, this centre possessing a motion of translation. It follows from the definition of the center of gravity that the components of the rotational motion, $\Sigma r \delta m$, for any given direction must equal zero. Hence in the transfer of energy during collisions we need not take into account the rotational motion of the systems colliding when the number of collisions are large and the average result alone is considered.

*b*. The average velocity of the centre of gravity can be calculated by equation 15 the molecular weight being known.

*c*. We can consider the number of impacts upon any infin-

itesimal of surface as being practically infinite and can resolve these forces into components in the plane of the surface and perpendicular to this plane. The components lying within the plane must cancel. The components perpendicular to the plane will have a certain average resultant R'. This average resultant is therefore the only force which we need to consider.

*d.* It is clear that since these resultants are very numerous they will hit the system at an average distance c' from the centre of gravity.

*e.* Assume the systems to be rigid. Let $m$ be the mass of each system. Then from mechanics the velocity of translation of the center of gravity will be $\frac{R'}{m}$ and the angular velocity about the center of gravity will be $\frac{R'c'}{mq^2}$, where $q$ is the radius of inertia about the center of gravity. Since the energy of the body will be the sum of the energy of translation about the center of gravity and the energy of rotation around the center of gravity, the total energy of the body will be, $E = \frac{1}{2} mv'^2 + \frac{1}{2} I\omega^2$, where $I = mq^2$ and $\omega$ = angular velocity. We will have,

$$E = \tfrac{1}{2} \frac{mR'^2}{m^2} + \tfrac{1}{2} mq^2 \frac{R'^2 c'^2}{m^2 q^4} = \tfrac{1}{2} \frac{R'^2}{m} + \frac{R'^2 c'^2}{mq^2}. \quad \text{Whence,}$$

$$\tfrac{1}{2} \frac{R'^2}{m} = \frac{q^2}{q^2 + c'^2} E = \text{Energy of translation} = E_4.$$

$$\text{And } \tfrac{1}{2} \frac{R'^2 c'^2}{m^2 q^2} = \frac{c'^2}{q^2 + c'^2} E = \text{Energy of rotation} = E_5.$$

$\therefore$ dropping primes, $\frac{E_5}{E_4} = \frac{c^2}{q^2}$. Since the system was supposed rigid $E_4 = E_5$ and the ratio of,

21. $\frac{E_i}{E_4} = \frac{E_5}{E_4} = \left(\frac{c}{q}\right)^2 = \frac{5-3\gamma}{3(\gamma-1)}$, from equation 20.

A decrease in $\gamma$ will correspond to a decrease in $q$ or an increase in $c$. Now $q$ is decreased by placing the heavy particles near the center of the system and increased when the reverse is true Supposing $c$ to remain constant we can make a first test of the supposition with which we began.

Comparing the system (see table 3) HOH with HSH we find that when oxygen is replaced by sulphur $\gamma$ increases from 1.2793 to 1.2913. It should decrease. Again comparing OCO with OSO, $\gamma$ decreases from 1.2947 to 1.2554. Also comparing $CH_4$ with $CHCl_3$ we find a decrease in $\gamma$ from 1.3175 to 1.122, when $\gamma$ should increase if heavy atoms are placed on the outside of the group. Even if $c$ be also supposed to vary it would have to increase enormously to balance the above decrease in $\gamma$. A further examination of the gases shown in Table 3 likewise shows a complete failure to confirm the formula derived above.

Since $c$ depends upon the shape and size of the surface presented to other colliding molecules we give below the calculations of O. E. Meyer [116] as to this "relative" surface presented by several atoms and from this data, since molecular surface is found to be the sum of the atomic, we can roughly guess at the variation in $c$.

Hydrogen = 5082, Oxygen = 8877, Nitrogen = 9513,
Carbon = 9796, Chlorine = 19513, Sulphur = 19617.

From a large number of investigated gases Meyer concluded in general that molecules have a shape that is flat and not spread out on all sides into space. We may use this condition to show still more clearly the failure of the above supposition to account for the internal energy of the molecule.

Assuming the density of the figure to be everywhere the same, we have for a rod of length $l$

$$q^2 = \frac{l^2}{12}, \quad c = \frac{l}{4}, \quad \text{Whence } \frac{E_5}{E_4} = .75.$$

For a rectangle having diameters $l$ and $l_1$

$$q^2 = \frac{1}{12}(l^2 + l_1^2), \quad c = \left(\frac{l^2 + l_1^2}{16}\right)^2, \quad \text{Whence } \frac{E_5}{E_4} = .75$$

Circular disc of radius $a$

$$q^2 = \frac{1}{2}a^2, \quad c = \frac{2}{3}a. \quad \text{Whence } \frac{c^2}{q^2} = \frac{8}{9} = .888.$$

Comparing these results with the ratio of $\frac{E_i}{E_4}$ shown in column 10, Table 3, we have only an occasional accidental correspondence and usually a disagreement so pronounced that no reasonable supposition as to the distribution of density would harmonize the results. For instance it will be seen that the ratio $\frac{E_i}{E_4}$ rises sometimes as high as 21 and it is almost impossible to conceive of a system in which $c$ is so large and $q$ so small that the above ratio should hold; for if the system be circular in shape then $q$ would have to be only about one seventh of the radius of the circle.

Abandoning the idea that molecules as a whole are rigid and capable of rotating we can give a different interpretation to the fact that monatomic molecules require no internal energy. For mechanically the idea that a body, other than a sphere, could be subject to collisions and yet not rotate can be explained by the supposition that molecules never really collide in the sense of an actual material contact, but that such coutact is prevented by a repulsive force.

Suppose then that the nature of a collision is such that the molecule as a whole has no tendency to rotate. Its atoms occupy definite positions within a "molecular sphere" and are affected only indirectly by the molecular collisions.

This idea of a molecule is suggested by the idea of "valence and bonds," also physical isomerism, optical affects, and all of those phenomena which are best explained by assuming a permanent configuration of the molecule.

The supposition is the reverse of the first as regards the internal energy. There we attempt to account for *all* of the internal energy as rotational energy of the molecule. Here we assume that the rotational energy of the molecule as a whole is zero.

A definite configuration of the molecule is consistent with either of two ideas. *a*. The atoms themselves possess no kinetic energy. Whatever energy they may have is entirely energy of position. *b*. The atoms are in motion, their energy being partly kinetic and partly potential. That all of the energy could not be kinetic Clausius has shown,[148] proving that such a system could not be stable.

The above ideas will appear more clearly if a third view of the molecular structure be here mentioned. (This view may also be consistent with a definite molecular structure.) The molecule with its atoms comprises a system such as the solar system having a motion of translation as a whole and its parts, while held together by attractive forces, yet possessing distinctive motion. The atoms are really separate entities, each capable of collision and while during a collision the nearness of the others will undoubtedly produce an effect yet the collision is primarily a collision of distinct particles. The translational motion of the system as a whole exists only as a certain portion of the motion of the separate atoms and in order to determine the energy of an atom the entire energy of the molecule must be divided by the number of atoms.

The other view above outlined supposes a molecule to be more than a mere collection of parts. It enters into collision as a whole and responds to a collision as a whole. Then to get the motion of each atom only the internal energy of the molecule $E_i$ must be divided among the the atoms.

It was by using this difference between the two views that an attempt was made to obtain a pointer as to which was correct. Column 9, Table 3, shows $E_i$ divided by the number of atoms. The results are shown plotted in line 2, Diagram 2. Column 11, Table 3, shows $\sigma_v \times m$ divided by the number of atoms. The results are shown plotted in line 3, Diagram 2.

In both lines the ordinates are drawn to twice the scale of line 1. It will be seen, comparing either line with line 1 that the irregularities of the latter are very much smoothed out. In line 3 there are only about eleven of the fifty-eight that fail to come between the limits 1.50 and 3.00 and line 2 is only slightly more irregular. This regularity was the basis for the remark (page 16) that $\gamma$ depended primarily on the number of atoms in the molecule.

That another factor needs also to be considered the irregularities of the lines 2 and 3 show as clearly. Comparing these lines with each other it was hoped to find one line distinctly more regular than the other, the more regular line belonging of course to the correct supposition. However neither line has any very marked advantage. If from line 2 the monatomic gases be omitted, and this is justifiable because the better view is that they have no internal atoms and hence no place in the diagram, this line has at first somewhat the advantage over line 3, but later it shows more marked irregularities. On the whole line 3 is more regular and in this line the monatomic gases find a place.

Examining line 3 in detail $AsCl_3$, $PCl_3$, $TiCl_4$, $CCl_4$ $SnCl_4$, $SiCl_4$, $C_2H_3Cl_4$, $CHCl_3$, $Cl_2$, $Br_2$ BrI, and $CS_2$ are above 2.978. That is, each atom of these molecules possesses more energy than the entire kinetic translational motion of the molecule to which they belong. Of these compounds only $CS_2$ fails to contain a halogen and this fact is at once suggestive of the idea that the atomic heat depends *upon the nature of the atoms.*

In pursuance of this idea $CH_4$, $C_2H_4$, $C_3H_6O_2$ (ethyl formate) and $C_3H_6O_2$ (methyl acetate) are the only gases that have an atomic energy below 1.500 and they all contain light hydrogen atoms $NH_3$, $H_2O$, $C_2H_2$, $C_3H_5Cl$, $C_2H_4Cl_2$ (ethylidine chloride). $C_2H_5Br$ and $C_2H_5Br$ show an atomic energy between 1.900 and 1.500. In these groups the high atomic energy of the halogens might be overbalanced by the low atomic energy of the hydrogen.

If atomic energy is a constant depending upon the atom then isomeric molecules should show the same energy. In reality we have,

| | | $E_i$ | $\sigma_v$ |
|---|---|---|---|
| $C_2H_5OH$ | alcohol | 1.754 | 2.082 |
| $(CH_3)_2O$ | ether | 1.662 | 1.991 |
| $C_3H_6O_2$ | ethyl formate | 1.176 | 1.445 |
| $C_3H_6O_2$ | methyl acetate | 1.040 | 1.308 |
| $C_2H_4Cl_2$ | ethylene chloride | 2.197 | 2.567 |
| $C_2H_4Cl_2$ | ethylidene " | 1.469 | 1.84 |

$E_i$ is taken from column 9 Table 3.
$\sigma_v$ " " " " 11 " 3.

The evidence is against the conclusion of equality but is hardly sufficient to be final.

If the energy of an atom is a constant quantity then the atomic energy of HCl should be the sum of the atomic energy of a hydrogen and a chlorine atom and so on. Below we show the result of such a calculation for several gases. Neither in these nor in other cases is there any evidence that the molecular energy is an additive property.

| | From $\sigma_v$ | | From $E_i$ | |
|---|---|---|---|---|
| | Observed | Calcula'd | Observed | Calcula'd |
| HCl | 4.916 | 5.649 | 1.956 | 2.691 |
| HBr | 5.616 | 5.831 | 1.659 | 2.874 |
| HI | 5.008 | 5.665 | 2.050 | 2.707 |
| BrI | 5.980 | 6.654 | 3.020 | 3.697 |
| ClI | 6.276 | 6.472 | 3.318 | 3.514 |

Boltzmann from theoretical grounds concluded[140] that the energy of an atom must be equal to the mean energy of trans-

latory motion of a molecule. But the conclusion was not justified as appears at once from line 3. Only eighteen out of the fifty-eight show approximately this much, or more energy.

O. E. Meyer states,[150] it seems to me the true view of the case, but he does not draw therefrom the conclusion which seems to me justified. The energy of an atom must be made up two of parts, its energy of position, due to chemical affinity, that is potential energy, and its energy of motion, kinetic energy. When the kinetic energy is great enough to overcome the residual affinity the molecules decompose. From these and similar considerations Meyer draws the conclusion that the mean energy of an atom must be less than the average molecular translatory energy. He explains the eight exceptions, seven being chlorine compounds (fourteen according to above table, all but one halogen compounds) as due to the fact that some of the heat was required to "disgregate" the molecules into simpler molecules. Were the temperature raised high enough to show no molecular association then the exceptions would disappear.

The conclusion which appears to me justified can be seen by considering the substances after they have been raised to such a temperature that the molecules have decomposed. That is to the temperature when the atoms *averaged* have just too much energy to be held by the average attraction upon the atom in its average position. At this point the kinetic energy of the atom is that required by the temperature and in addition to this energy the atoms possess the energy of position due to the chemical attraction. Hence in dissociating a compound, *eventually* to just effect the decomposition, more energy, by an amount equal to the energy of position of the atoms, must be given to the atoms than is possessed by the molecule as translatory motion.

That this energy is not, like the latent heat of vaporization, supplied to the molecule at one definite temperature is a well known fact of which even extensive industrial use has been

made. To illustrate, the energy electrically neccessary to decompose NaCl is not the same at its fusion point that it is at the ordinary temperature, but is much less, due to the fact that the heat added in raising the compound to its point of fusion is spent partly in aiding its decomposition.

It seems to me clear that the limit of the energy of an atom while in a compound is not the energy of translatory motion of the molecule but an amount just twice this, and it is finally made up of two parts, half kinetic and half potential. Of these two parts the kinetic probably, though of this there is no direct evidence except the rough constancy of line 3, is added gradually and is a function of the temperature. The potential is added more or less rapidly according to the individual nature of the molecule.

Since a study of the specific heat per degree only indicates how rapidly the energy is added to the atom I can see no reason why it should not show, as it does, sometimes an energy increment per atom two or three (quite possibly more) times as great as the increment of translatory motion per molecule. *According to this view a high specific heat per atom indicates only that the potential energy of the atoms is being rapidly increased and that the molecule is approaching the point of dissociation.* In fact a study of the change in the specific heat per atom will enable one to calculate when complete disassociation will take place and the determination of this point will also give us an actual measure of the chemical affinity.

From this point of view the irregularities of line 3 are quite explicable. Halogen compounds as a rule show a high heat per atom because they are more nearly approaching the point of dissociation. It is noteworthy that the other compound showing excessive atomic energy is $CS_2$ an exothermic body and chemically not very stable.

Again referring to the general ideas set fort has to the molecular structure, is it not possible that what we have been calling the kinetic translational energy of the molecule is really the amount of energy exchanged by a collision of two systems

and is dependent upon other factors than the temperature. That is, if the atoms within the molecule have various motions, may it not happen that the collision is of such a character that the average amount of energy exchanged is not the same as would be due to the assigned average forward motion of the molecules?

The most conclusive answer to such a question is the fact that sound travels with just the velocity that it should possess if its propagation is due to the assigned speed of the molecules. Also Boltzmann[151] extended Maxwell's conclusions to compound molecules showing that atomic motion does not alter the conclusions derived therefrom. This coupled with what has been said above concerning approaching molecular decomposition leads to the rejection of the idea that all of the atomic energy could possibly be potential.

To think of a molecule as a miniature world system is mechanically the most reasonable supposition and all of the evidence above mentioned, so far as it carries any weight, strengthens this idea of the molecular structure.

### B. THE LATENT HEAT OF VAPORIZATION.

It is a commonplace fact that energy is always required to change a liquid into a gas the temperature remaining constant. We have already called attention to the fact that the modern theory of solutions makes it necessary to conclude that the molecule of a liquid possesses on the average the same amount of kinetic translational energy as the molecule of a gas at the same temperature. Also the facts which we have discussed at length above point clearly to the fact that the internal energy of a molecule for slight changes of temperature (that is so long as the molecule itself suffers no change) is practically a function of the translational energy of the molecule. We must conclude therefore that the energy *per se* of a molecule must be the same in the liquid as in the gaseous state. If at a given temperature a given weight of gas represents more energy than the same weight of the sub-

stance as a liquid, the extra energy of the gas must be energy of position only. It cannot be held to be energy of motion so long as the gas law, $PV = RT$, be found true for solutions without surrendering all that is essential in the kinetic theory of gases.

The energy which is added to change a liquid into a gas must then be spent *solely* in overcoming the external pressure and in altering the distance apart of the molecules, (unless the molecule breaks apart also).

Continuing the notation already adopted the energy spent in overcoming the external pressure is denoted by $E_1$ and this energy can be easily calculated, equation 4.

The energy spent in overcoming the molecular attraction is denoted by $E_3$ and the total "latent" heat supplied by $L$. Therefore we have,

22. $L - E_1 = E_3$.

In the theory of liquids it is usual to consider molecular action upon any individual molecule as limited to a certain sphere around that molecule.

Imagine such a molecular sphere. If the molecules contained therein are very numerous we can suppose them evenly distributed around the central molecule. Suppose an expansion of the system to take place so that the molecules formerly contained in this sphere are now evenly distributed throughout a larger sphere. Let $v$ and $V$ represent the volumes of the two spheres and $n$ the number of molecules. Then the distances between the molecules of the two spheres are $\left(\frac{v}{n}\right)^{1/3}$ and $\left(\frac{V}{n}\right)^{1/3}$ respectively. *Now assuming that the attraction between the molecules varies inversely as the square of the distance apart of the molecules we can derive a means of testing the assumption as follows:—*

Let a certain molecule be distant from the central molecule by $x\left(\frac{v}{n}\right)^{1/3}$ before expansion. After expansion the same

molecule must be distant $x\left(\frac{V}{n}\right)^{\frac{1}{3}}$ The energy spent in moving this molecule against the attraction of the central molecule is, from mechanics,

23.

$$m\mu\left\{\frac{1}{x\left(\frac{v}{n}\right)^{\frac{1}{3}}}-\frac{1}{x\left(\frac{V}{n}\right)^{\frac{1}{3}}}\right\}=\frac{m\mu}{x}\left\{\frac{1}{\left(\frac{v}{n}\right)^{\frac{1}{3}}}-\frac{1}{\left(\frac{V}{n}\right)^{\frac{1}{3}}}\right\}$$

where $m$ is the mass of the molecule and $\mu$ the absolute attraction at unit distance from the central molecule.

If we in turn consider similarly the energy spent in moving each molecule of the sphere and sum up, we have for the total energy necessary to overcome the attraction of the central molecule in producing the given expansion

24. $$E_m=m\mu\left\{\frac{1}{\left(\frac{v}{n}\right)^{\frac{1}{3}}}-\frac{1}{\left(\frac{V}{n}\right)^{\frac{1}{3}}}\right\}\left(\frac{1}{x}+\frac{1}{x_1}+..+\frac{1}{x_{n-2}}\right)$$

This latter factor we will call $c'$.

This expression represents the energy spent by the molecule of the mass in moving away from a single molecule during a given expansion. Hence to get the total energy of expansion for a given mass $M$ we must multiply the above expression by one half the number of molecules, since from the form of the solution of each pair of molecules compared one only is considered moved. Putting

$$mn=M,\ \frac{c'}{2}=c,\ v=\frac{m}{d}=\frac{mn}{d},\text{ and } V=\frac{mn}{D},\text{ we have,}$$

25. $$E_M=\frac{M\mu c}{m^{\frac{1}{3}}}(d^{\frac{1}{3}}-D^{\frac{1}{3}}).$$ Where $E_M$ is the energy

necessary to produce the expansion in mass $M$ from density $d$ to $D$, $m$ being the molecular weight of a molecule and $\mu$ the absolute attraction. $c$ is an unknown constant.

If we consider this last equation to hold during the change of volume of a liquid into a gas at temperature $T$ then we have referring to equation 22,

26. $L_T - E_{,T} = \frac{M\mu c}{m^{1/3}}\left(d_T^{1/3} - D_T^{1/3}\right)$, and at $t$,

$L_t - E_{,t} = \frac{M\mu c}{m^{1/3}}\left(d_t^{1/3} - D_t^{1/3}\right)$. Now making the supposition that $\mu$ remains constant with the temperature we obtain the ratio of the two equations

27. $\frac{L_T - E_{,T}}{L_t - E_{,t}} = \frac{d_T^{1/3} - D_T^{1/3}}{d_t^{1/3} - D_t^{1/3}}$, an equation in which all of the quantities can be measured, *and which therefore affords an experimental test of the assumptions that the molecular attraction varies inversely as the square of the distance from the molecule and does not vary with the temperature.*

The result of this test is shown in Table 5. Columns 1 to 7, contain the data with the citations of authority. The latent heats are referred to water 0° to 1° C. as the standard calorie. This was taken to be 1.007 of the standard assumed.

Column 9 gives $E_{,}$ calculated from equation 7, divided by 1.007, which gives,

28. $E_{,} = .024(V - v)p$ Cals., $p$ being in atmospheres.

Column 10 gives the two temperatures $T$ and $t$ concerned in the calculations which follow on the same line. The ratio of $\frac{L_T - E_{,T}}{L_t - E_{,t}}$ is given in column 11 and the ratio of $\frac{d_T^{1/3} - D_T^{1/3}}{d_t^{1/3} - D_t^{1/3}}$

is given in column 12. No actual determinations of the density of the gas could be obtained for $CH_3OH$, $C_2H_5OH$, $(C_2H_5)_2O$, $CS_2$, $C_6H_6$, and $CCl_4$ at the desired temperatures. The density was therefore calculated for these gases from the equation

29. $D_t = \frac{.01227\ p \times m}{t}$, based on the gas laws and the density of hydrogen already given[2]. The error thus introduced is probably very small, since for the indicated pressure the gases if normal obey the gas laws closely.

Of the twenty ratios shown from ten different substances in columns 11 and 12 only three, $N_2O$ from —20° to 0°, and from —20° to 20°, $SO_2$ from 0° to 65°, fail to agree by as much as 6 per cent. The agreement of the ratios shown may be regarded on the whole as quite satisfactory, since eight measurements, some of them difficult, enter into each calculation, thus making the probable error of observation quite large.

It will be noticed however that within the limits for which equation 27 is tested we are really getting on both sides of the equation the ratio of two numbers which are very nearly equal, and from this standpoint the agreement might appear to be quite accidental. It becomes necessary therefore to look at the subject from a different point of view.

If the ideas which have been presented are correct then at temperature $T$, $L_T - E_{,T}$ represents the energy required to produce a given change in the density of the substance. At temperature $t$ a different change in the density of the substance occurs. How much latent heat will now be required to produce this new change in the density, if the law of attraction is the inverse square of the distance? Or in other words—the latent heat of a substance changes with the temperature. How much of the change can be accounted for on the supposition that it is caused solely by the corresponding change in the density of the body the attraction to vary as described viz., inversely with the distance apart of the molecules?

We must have,

30. $(L_T - E_{,T}) - (L_t - E_{,t}) =$ Change in latent heat with the temperature, as an observed fact simply. Since from equation 27, $L_t - E_{,t} = \frac{(L_T - E_{,T})(d_t^{\frac{1}{3}} - D_t^{\frac{1}{3}})}{d_T^{\frac{1}{3}} - D_T^{\frac{1}{3}}}$, we also have,

31. $(L_T - E_{,T}) - \frac{(L_T - E_{,T})(d_t^{\frac{1}{3}} - D_t^{\frac{1}{3}})}{d_T^{\frac{1}{3}} - D_T^{\frac{1}{3}}} =$ Change in latent heat calculated upon the supposition that the attraction varies as the inverse square of the distance apart of the molecules.

Or combining the two equations,

32. $(L_T - E_{,T}) - (L_t - E_{,t})$

$$= (L_T - E_{,T}) - \frac{(L_T - E_{,T})(d_t^{\frac{1}{3}} - D_t^{\frac{1}{3}})}{d_T^{\frac{1}{3}} - D_T^{\frac{1}{3}}}.$$

In Table 5, column 13, gives the observed differences as shown by equation 30. Column 14 gives the calculated change in the latent heat as shown by equation 31. Column 15 gives the differences between the two values, the calculated being subtracted from the observed.

In eight out of the twenty comparisons the error is more than three cals. And in four cases $H_2O$ 0° to 100°, 0° to 200°, 100° to 200°, and $C_2H_5OH$ 0° to 78°, is the error more than 5 cals. The following points are to be noted:

1. By the subtraction, the sum total of the error introduced by all the measurements is left in the result. This tends to magnify an error *relatively* small.

5. A study of the measurements entering into the calculation and a comparison of these and similar measurements which have been made will show that an error of three cals.

is easily within the limits of error of the measurements as taken. Even an error of four cals. is not excessively large. For instance different measurements of the latent heat of water at 0° and at 100° show an error by difference of 21 cals. Alcohol which shows the next largest variation, column 15, shows similarly a possible error of 6.5 cals. As to $N_2O$, the third largest variation, an inspection of the values used shows that the density measurements are irregular and somewhat uncertain. Possibly the failure to agree in this case is due to these measurements.

3. The attraction was assumed constant, it may vary slightly owing to the loosening of the chemical bonds etc.

4. No allowance was made for molecular association or dissociation. Even if such association is caused by the attraction which we are considering, yet it would modify the value of $E_1$ and would thus produce quite an appreciable effect. Also the method employed to calculate the average distance apart of the molecules would not hold good.

5. The fact that in the case of $N_2O$, agreement is reached in one case would seem to indicate either an error in some measurement, for the other cases, or else the existence of some temporary condition, as molecular association, causing the variation.

6. *The general correspondence of the two sets of values is too marked to be accidental.* In the case of water certainly, and probably in several other cases, the disagreement is too pronounced to be laid upon the experimental error. It may be that one or several of the causes above mentioned are sufficient to explain the discrepancies.

By reference to equation 26 and the supposition there made it will be seen that $\frac{M\mu c}{m^{\frac{1}{3}}} = \text{constant}$ and we can therefore write the equation,

33. $L_T - E_{1T} = C\,(d_T^{\frac{1}{3}} - D_T^{\frac{1}{3}})$. But this is the equation of a *straight line through the origin of coordinates* if $L - E_1$

TABLE 5.

| 1 FORMULA | 2 Molecular Weights | 3 Temperature Degrees C. | 4 Pressure in Atmosphere | Authority | 5 Density of Liquid | Authority | 6 Density of Gas | Authority | 7 Latent Heat | Authority |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$ | 17.88 | 0 | .006 | 155 | .99987 | 156 | .00000475 | 157 | 597.6 | 158 |
| | | 100 | 1 | | .95865 | | .00060621 | | 535.0 | |
| | | 200 | 15.38 | | .8637 | | .0079555 | | 464.3 | |
| $CH_3OH$ | 31.78 | 0 | .0372 | 165 | .816 | 168 | .0000531 | | 289.17 | 172 |
| | | 66 | 1 | 167 | .748 | 169 | .00115 | | 265.67 | 171 |
| | | 100 | 3.165 | 166 | .7134 | 170 | .00331 | | 246.01 | 172 |
| $CO_2$ | 43.66 | —25 | 17.12 | 159 | 1.025 | 160 | .044 | 160 | 72.23 | 161 |
| | | 0 | 35.40 | | .905 | | .097 | | 56.86 | |
| | | 22.04 | 61.75 | | .725 | | .220 | | 31.80 | |
| $N_2O$ | 43.74 | —20 | 23.14 | 152 | .996 | 153 | .044 | 153 | 66.90 | 154 |
| | | 0 | 36.08 | | .902 | | .081 | | 59.50 | |
| | | 20 | 55.30 | | .755 | | .151 | | 43.25 | |
| $C_2H_5OH$ | 45.68 | 0 | .0164 | 186 | .8075 | 188 | .0000336 | | 236.5 | 190 |
| | | 78.2 | 1 | 187 | .7374 | 189 | .001595 | | 205.7 | 191 |
| $SO_2$ | 63.6 | 0 | 1.52 | 162 | 1.434 | 163 | .00447 | 163 | 91.45 | 164 |
| | | 30 | 4.56 | | 1.352 | | .0136 | | 80.5 | |
| | | 65 | 12.11 | | 1.245 | | .0361 | | 68.4 | |
| $(C_2H_5)_2O$ | 73.48 | 0 | .243 | 192 | .736 | 194 | .000802 | | 93.75 | 196 |
| | | 34.9 | 1 | 193 | .696 | 195 | .00293 | | 88.88 | 197 |
| $CS_2$ | 75.56 | 0 | .1683 | 180 | 1 295 | 182 | .000572 | | 89.75 | 184 |
| | | 46.2 | 1 | 181 | 1.225 | 183 | .00291 | | 85.24 | 185 |
| $C_6H_6$ | 77.4 | 0 | .0342 | 198 | .899 | 200 | .000119 | | 109.00 | 202 |
| | | 80.4 | 1 | 199 | .8127 | 201 | .00268 | | 93.18 | 203 |
| $CCl_4$ | 152.62 | 0 | .0434 | 173 | 1.631 | 176 | .000298 | | 52.00 | 178 |
| | | 76.5 | 1 | 174 | 1.480 | 177 | .00536 | | 46.35 | 179 |

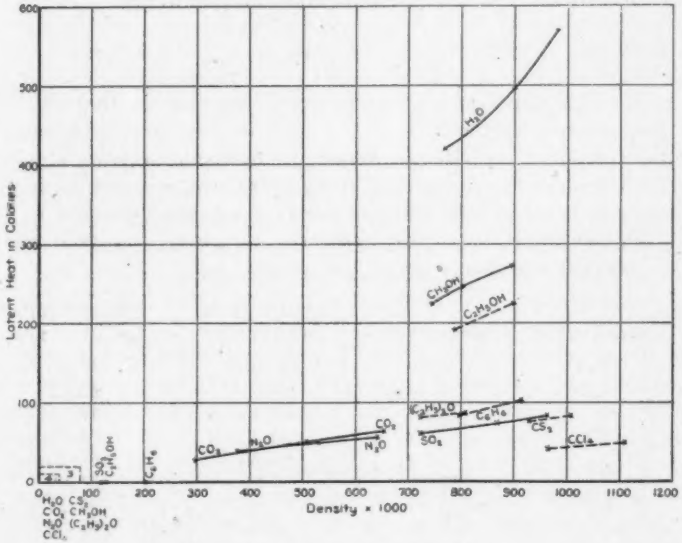
ABLE 5.

| 7 Heat | Authority | 8 Latent Heat Calculated | 9 $E_t$ | 10 Temperature Degrees C. | 11 Ratio $\frac{L_T - E_{1T}}{L_t - E_{1t}}$ | 12 Ratio $\frac{d_T^{\frac{1}{3}} - D_T^{\frac{1}{3}}}{d_t^{\frac{1}{3}} - D_t^{\frac{1}{3}}}$ | 13 Observed | 14 Calculated | 15 Observed Minus Calculated |
|---|---|---|---|---|---|---|---|---|---|
| 7.6 | 158 | | 30.34 | 0, 100 | 1.15 | 1.090 | 71.9 | 47.2 | 24.7 |
| 5.0 | | 559.7 | 39.57 | 0, 200 | 1.35 | 1.305 | 149.0 | 133.2 | 15.80 |
| 4.3 | | 480.1 | 45.99 | 100, 200 | 1.18 | 1.199 | 77.1 | 86.0 | —8.90 |
| 9.17 | 172 | | 16.81 | 0, 66 | 1.112 | 1.117 | 27.53 | 28.55 | —1.02 |
| 5.67 | 171 | 264.65 | 20.84 | 0, 100 | 1.220 | 1.205 | 49.20 | 46.31 | 2.89 |
| 6.01 | 172 | 248.90 | 22.85 | 66, 100 | 1.096 | 1.078 | 21.67 | 17.75 | 3.91 |
| 2.23 | 161 | | 8.94 | —25, 0 | 1.290 | 1.290 | 14.25 | 14.21 | .04 |
| 3.86 | | 56.90 | 7.82 | —25, 22 | 2.334 | 2.213 | 36.18 | 34.79 | 1.39 |
| 1.80 | | 33.19 | 4.69 | 0, 22 | 1.809 | 1.721 | 22.93 | 20.58 | 2.35 |
| 5.90 | 154 | | 12.07 | —20, 0 | 1.102 | 1.210 | 5.06 | 9.52 | —4.46 |
| 9.50 | | 55.04 | 9.73 | —20, 20 | 1 514 | 1.707 | 18.61 | 22.72 | —4.11 |
| 3.25 | | 39.14 | 7.03 | 0, 20 | 1.374 | 1.411 | 13.55 | 13.20 | .35 |
| 5.5 | 190 | | 11.71 | 0, 78 | 1.18 | 1.143 | 34.13 | 28.29 | 5.84 |
| 5.7 | 191 | 211.54 | 15.04 | | | | | | |
| 1.45 | 164 | | 8.14 | 0, 30 | 1.149 | 1.110 | 10.78 | 8.31 | 2.47 |
| 9.5 | | 82.97 | 7.97 | 0, 65 | 1.375 | 1.291 | 22.73 | 18.77 | 3.96 |
| 8.4 | | 73.67 | 7.82 | 30, 65 | 1.197 | 1.162 | 11.95 | 10.46 | 1.49 |
| 3.75 | 196 | | 7.26 | 0, 34 9 | 1.071 | 1.090 | 5.77 | 7.15 | —1.38 |
| 8.88 | 197 | 87.50 | 8.17 | | | | | | |
| 9.75 | 184 | | 7.06 | 0, 46.2 | 1.074 | 1.086 | 5.69 | 6.57 | —.88 |
| 5.24 | 185 | 84.35 | 8.23 | | | | | | |
| 9.00 | 202 | | 6.90 | 0, 80.4 | 1.212 | 1.153 | 17.85 | 13.60 | 4.25 |
| 3.18 | 203 | 97 43 | 8.94 | | | | | | |
| 2.00 | 178 | | 3.50 | 0, 76.5 | 1.157 | 1.150 | 6.61 | 6.33 | .28 |
| 6.35 | 179 | 46.63 | 4.46 | | | | | | |

and $d^{1/3} - D^{1/3}$ be regarded as the variables. This gives us a method of showing to the eye the approximation of the formula.

In Diagram 3, $L - E_1$ are plotted as ordinates and $d^{1/3} - D^{1/3}$ as abscissa. When three observations were shown as in the case of $N_2O$, $H_2O$, $CO_2$, $SO_2$ and $CH_3OH$ the dots are connected by a heavy line. *It will be seen that the curvature of these*

DIAGRAM 3.




*lines is but slight.* Where only two observations were available the observations are connected by a dotted line. If these lines are prolonged four, $H_2O$, $CO_2$, $N_2O$, $CCl_4$, will enter the small square outlined around the origin. Three others $CS_2$, $CH_3OH$, $(C_2H_5)_2O$, come within the second square, and the end, if prolonged of $SO_2$, $C_6H_6$ and $C_2H_5OH$ are shown by dots.

*The diagram shows how strikingly improbable is the supposition that the relations given are accidental.*

Since equations 27, 32, 33, are but altered expressions of the same fact, we cannot regard them as helping to confirm each other. They only serve to emphasize the agreement originally shown, equation 27. But if we can confirm the above results by an altogether different argument, then we very much increase the probability that both the original hypothesis and the conclusions derived therefrom are true.

Such a confirmation we can obtain by the help of a theorem by Crompton[205] where the following relation holds

$$34. \qquad L_T = 2RT \log_e \frac{d}{D}.$$

An equation which is very neatly derived on theoretical grounds quite different from the above assumptions. (Crompton considers the change in density as due to pressure alone, then doubles the amount of energy required, in order to keep the substance in that state without the excess of pressure).

In comfirmation of this result the following observed and calculated latent heats were given:

| SUBSTANCE. | TEMPERATURE. | LATENT HEAT OBSERVED. | LATENT HEAT CALCULATED. |
|---|---|---|---|
| $N_2O$ | —20 | 66.90 | 70.93 |
| | 0 | 59.50 | 58.77 |
| | 20 | 43.25 | 42.36 |
| $CO_2$ | —25 | 72.23 | 71.91 |
| | 0 | 56 86 | 54.26 |
| | 22.04 | 31.80 | 31.09 |
| $SO_2$ | 0 | 91.45 | 97.17 |
| | 30 | 80.5 | 86.05 |
| | 65 | 68.4 | 70.03 |

The calculated latent heats show undoubted correspondence to the observed values and the lack of exact agreement is attributed by Mr. Crompton to molecular association.

It seemed to me that the theory was hardly well enough established by the published results shown above to warrant its

use for the purpose in view, where it could not be checked by experiment, As a preliminary to its use a further examination of the theory was undertaken. The values given by Mr. Crompton were recalculated from the data used as above shown, Table 5, and below, Table 6, column 7, are given the values obtained. They are practically the same as those given by Mr. Crompton. Also the value for water for which data were found at the temperatures 0°, 100°, 200° C. are added. For all of the other substances shown below the calculated density of the gas is used, equation 29, because the substance could be assumed, *within the limits of pressure used, to obey the gas laws very accurately, provided molecular association did not take place.* If there were such association Mr. Crompton's theory, unmodified as to the molecular weight could not be used properly and hence this calculation introduces no new assumption.

Columns 1 to 4, Table 6, show the data used and cite authority except for the substances already given in Table 5. Column 5 contains the calculated density of the gas. Column 6 the observed latent heat and Column 7 the calculated.

Twenty-five gases are shown and forty comparisons are obtained. In twenty-one of these comparisons the agreement is within five per cent. In ten others within ten per cent. Nine are off more than ten per cent. This would seem to be a not very good agreement but several points must be noticed. The calculated latent heats are usually the largest, in every case when the theoretical density is used, except $C_2H_5OH$ at 78.2° and $C_3H_6O_2$, methyl acetate, at 56.3°. This was to be expected since the theoretical density of the gas used would be somewhat too small. Again it will be noticed that the agreement is better if the comparisons at the boiling points of the substance are alone considered. There are twenty-two such observations and of these fourteen are within five per cent of agreement and only four above ten per cent. These four are $H_2O$, $CS_2$, $C_2H_5OH$, and $C_2H_4O_2$ and all of them except $CS_2$ *are liquids whose molecules are known to be associated.*[251] The

amount of molecular assocition of a liquid has been found to increase with decrease of temperature and this would explain the fact that the agreement is not so good at temperatures below the boiling poiut. (For such molecular association would cause an energy change not contemplated by Crompton's formula. Besides if the association persisted in the gaseous state it would canse a variation from the calculated density of the gas. This latter observation does not apply to water where the observed density was available.)

It would seem that Crompton's theory can be regarded as giving very approximately correct results when molecular association does not take place.

If we consider any gas, it is reduced to the liquid state by pressure and by the molecular attraction. In nature of course the two, pressure and attraction, act jointly and continuously. But theoretically we can separate their action, since mechanically all forces are independent of each other. Legitimately then, we can consider a liquid at its critical temperature as reduced to that density: first, by the action of a pressure; second by the action of molecular attraction. Accordingly the theoretical density of the gas at its critical temperature and under its critical pressure was calculated from equation 29. *The gas would be reduced to that condition if there were no molecular attraction. The remainder of the condensation, to the actual density, must be the work of the attraction alone.*

If the attraction obeys the law already assumed viz., the inverse square of the distance, and if this attraction be supposed not to vary with the temperature we can use equation 27 to calculate the energy expended at the critical point by the attraction in changing the gas from its theoretical to its observed density. The theoretical density of the gas at the critical temperature $D_T = \frac{.01227\, p_T m}{T}$, (equation 29). Likewise $E_{,T} = .024\left(\frac{1}{D_T} - \frac{1}{d_T}\right) p_T = .024\left(\frac{T}{.01227\, p_T m} - \frac{1}{d_T}\right) p_T$,

TABLE 6.

| 1 SUBSTANCE | 2 Molecular Weight | 3 Temperature Degrees C | Authority | 4 Density of Liquids | Authority | 5 Density of Gas | 6 Latent Heat Observed | Authority | 7 Latent Heat Calculated |
|---|---|---|---|---|---|---|---|---|---|
| Water, $H_2O$ | 17.88 | 0 | | | | | 597.6 | | 733.00 |
| | | 100 | | | | | 535.0 | | 601.70 |
| | | 200 | | | | | 464.3 | | 484.30 |
| Methyl alcohol, $CH_3OH$ | 31.78 | 0 | | | | | 289.17 | | 325.36 |
| | | 66 | | | | | 265.67 | | 270.69 |
| | | 100 | | | | | 246.01 | | 246.99 |
| Carbon dioxide, $CO_2$ | 43.66 | —25 | | | | | 72.23 | | 70.00 |
| | | 0 | | | | | 56.86 | | 54.68 |
| | | 22 | | | | | 31.80 | | 31.60 |
| Nitrous oxide, $N_2O$ | 43.74 | —20 | Refer to Table 5. | Refer to Table 5. | | Refer to Table 5. | 66.90 | Refer to Table 5. | 70.62 |
| | | 0 | | | | | 59.50 | | 58.87 |
| | | 20 | | | | | 43.25 | | 42.22 |
| Ethyl alcohol, $C_2H_5OH$ | 45.68 | 0 | | | | | 236.5 | | 236.50 |
| | | 78.2 | | | | | 205.7 | | 184.70 |
| Sulphur dioxide, $SO_2$ | 63.6 | 0 | | | | | 91.45 | | 96.88 |
| | | 30 | | | | | 80.5 | | 85.72 |
| | | 65 | | | | | 68.4 | | 73.67 |
| Ethyl ether, $(C_2H_5)_2O$ | 73.48 | 0 | | | | | 93.75 | | 99.36 |
| | | 34.9 | | | | | 88.88 | | 89.76 |
| Carbon disulphide, $CS_2$ | 75.56 | 0 | | | | | 89.75 | | 109.21 |
| | | 46.2 | | | | | 85.24 | | 99.86 |
| Benzene, $C_6H_6$ | 77.4 | 0 | | | | | 109.00 | | 123.46 |
| | | 80.4 | | | | | 93.18 | | 102.17 |
| Carbon tetrachloride, $CCl_4$ | 152.62 | 0 | | | | | 52.00 | | 60.27 |
| | | 76.5 | | | | | 46.35 | | 50.62 |
| Acetic acid, $C_2H_4O_2$ | 59.56 | 118.1 | 61 | .935 | 62 | .00187 | 84.9 | 63 | 159.73 |
| Ethyl formate, $C_3H_6O_2$ | 73.46 | 54.0 | 64 | .870 | 65 | .00276 | 99.3 | 66 | 99.99 |
| Methyl acetate, $C_3H_6O_2$ | 73.46 | 56.3 | 67 | .8836 | 68 | .00274 | 102.1 | 69 | 101.39 |
| Ethyl acetate, $C_4H_8O_2$ | 87.36 | 75.2 | 70 | .8292 | 71 | .00308 | 86.68 | 72 | 87.23 |
| Methyl propionate, $C_4H_8O_2$ | 87.36 | 79.5 | 73 | .8445 | 74 | .00304 | 84.15 | 75 | 88.92 |
| Propyl formate, $C_4H_8O_2$ | 87.36 | 81.2 | 76 | .8242 | 77 | .00303 | 85.25 | 78 | 89.16 |
| Ethylidene chloride, $C_2H_4Cl_2$ | 98.16 | 57.6 | 79 | 1.1100 | 80 | .00364 | 67.02 | 81 | 75.33 |
| Ethyl propionate, $C_5H_{10}O_2$ | 101.26 | 98.6 | 82 | .7975 | 83 | .00334 | 77.1 | 84 | 78.69 |
| Isobutyl formate, $C_5H_{10}O_2$ | 101.26 | 98.5 | 85 | .7806 | 86 | .09335 | 77.0 | 87 | 78.78 |
| Methyl butyrate, $C_5H_{10}O_2$ | 101.26 | 101.9 | 88 | .8026 | 89 | .00331 | 77.25 | 90 | 79.65 |
| Propyl acetate, $C_5H_{10}O_2$ | 101.26 | 102 | 91 | .793 | 92 | .00331 | 77.3 | 93 | 79.46 |
| Ethyl butyrate, $C_6H_{12}O_2$ | 115.16 | 119.6 | 94 | .770 | 95 | .00360 | 71.5 | 96 | 71.64 |
| Ethyl isobutyrate, $C_6H_{12}O_2$ | 115.16 | 110.1 | 97 | .7726 | 98 | .00369 | 69.2 | 99 | 69.67 |
| Isobutyl acetate, $C_6H_{12}O_2$ | 115.16 | 116.5 | 100 | .7650 | 101 | .00363 | 69.9 | 102 | 70.86 |
| Methyl valerate, $C_6H_{12}O_2$ | 115.15 | 116.3 | 103 | .7767 | 104 | .00363 | 69.95 | 105 | 71.06 |

from equation 28, substituting these in equation 27 we have

$$35.\quad L_T - .024\left(\frac{T}{.01227\,p_T m} - \frac{1}{d_T}\right)p_T = \left\{\frac{d_T^{1/3} - \left(\frac{.01227\,p_T m}{T}\right)^{1/3}}{d_t^{1/3} - D_t^{1/3}}\right\} L_t - E_t$$

By the use of Crompton's theory, we can obtain another measure of the same amount of work and the two results should agree. In this case again writing for $D_T$ its value we have from equation 34,

$$36.\quad L_T = \frac{2\,RcT}{m}\log_e d_t - \log_e \frac{.01227\,p_T m}{T}, \text{ where } Rc = 1.958.$$

Or combining the two equations,

$$37.\quad \frac{3.916\,T}{m} - \left(\log_e d_T - \log_e \frac{.01227\,p_T m}{T}\right) - \left(.024\frac{T}{.01227\,p_T m} - \frac{1}{d_T}\right)p_T = \left\{\frac{d_T^{1/3} - \left(\frac{.01227\,p_T m}{T}\right)^{1/3}}{d_t^{1/3} - D_t^{1/3}}\right\}\left\{L_t - .024\left(\frac{1}{D_t} - \frac{1}{d_t}\right)p_t\right\}$$

and when $D_t$ is also calculated, equation 29, the equation assumes a still more complicated form.

In Table 7, column 9, contains the results calculated according to the left hand side of the equation 37, and column 10 contains the results calculated from the right hand side of the equation. When the necessary data could be obtained for the latter calculation at several different temperatures, the

TABLE 7.

| 1 SUBSTANCE | 2 Molecular Weight | 3 Critical Temperature C. | 4 Pressure in Atmosphere | 5 Critical Density | 6 Theoretical Density of the Gas. | 7 $L_T$ per Cromton. | 8 $E_{1T}$ |
|---|---|---|---|---|---|---|---|
| Water, $H_2O$ | 17.88 | 362.4 | 197.5 | .429 | .0680 | 256.4 | 58.63 |
| Carbon dioxide, $CO_2$ | 43.66 | 31.0 | 75.0 | .450 | .1322 | 33.37 | 9.64 |
| Nitrous oxide, $N_2O$ | 43.74 | 35.9 | 74.0 | .410 | .1286 | 32.07 | 9.47 |
| Ethyl alcohol, $C_2H_5OH$ | 45.68 | 236.8 | 64.23 | .2884 | .0706 | 61.47 | 16.47 |
| Sulphur dioxide, $SO_2$ | 63.6 | 156.6 | 78.9 | .505 | .1433 | 33.24 | 9.47 |
| Ethyl ether $(C_2H_5)_2O$ | 73.48 | 193.4 | 37.16 | .245 | .0718 | 30.55 | 8.76 |
| Carbon disulphide, $CS_2$ | 75.56 | 275.0 | 76.3 | .365 | .1290 | 29.49 | 9.18 |
| Benzene, $C_6H_6$ | 77.4 | 289.3 | 52.6 | .355 | .0888 | 39.59 | 10.66 |
| Acetic acid, $C_2H_4O_2$ | 59.56 | 321.5 | 57.1 | .4065 | .0702 | 68.62 | 16.14 |
| Ethyl formate, $C_3H_6O_2$ | 73.46 | 233.9 | 48.93 | .315 | .0870 | 34.73 | 9.77 |
| Methyl acetate, $C_3H_6O_2$ | 73.46 | 234.6 | 52.57 | .320 | .0933 | 33.36 | 9.58 |
| Ethyl acetate, $C_4H_8O_2$ | 87.36 | 248.6 | 40.92 | .2993 | .0840 | 29.69 | 8.41 |
| Methyl propionate, $C_4H_8O_2$ | 87.36 | 259.8 | 39.88 | .300 | .0802 | 31.51 | 8.74 |
| Propyl formate, $C_4H_8O_2$ | 87.36 | 262.9 | 42.7 | .305 | .0854 | 30.58 | 8.64 |
| Ethylidene chloride, $C_2H_4Cl_2$ | 98.16 | 254.8 | 52.45 | .419 | .1197 | 26.24 | 7.51 |
| Ethyl propionate, $C_5H_{10}O_2$ | 101.26 | 277.5 | 34.64 | .286 | .0781 | 27.61 | 7.74 |
| Isobutyl formate, $C_5H_{10}O_2$ | 101.26 | 278.2 | 38.29 | .288 | .0864 | 25.61 | 7.44 |
| Methyl butyrate, $C_5H_{10}O_2$ | 101.26 | 278.0 | 36.02 | .291 | .0812 | 27.19 | 7.71 |
| Propyl acetate, $C_5H_{10}O_2$ | 101.26 | 274.4 | 34.8 | .290 | .0790 | 27.51 | 7.69 |
| Ethyl butyrate, $C_6H_{12}O_2$ | 115.16 | 298.5 | 30.24 | .276 | .0748 | 25.31 | 7.07 |
| Ethyl isobutyrate, $C_6H_{12}O_2$ | 115.16 | 285.4 | 30.13 | .276 | .0762 | 24.41 | 6.87 |
| Isobutyl acetate, $C_6H_{12}O_2$ | 115.16 | 292.5 | 31.4 | .281 | .0784 | 24.54 | 6.92 |
| Methyl valerate, $C_6H_{12}O_2$ | 115.16 | 288.6 | 31.5 | .279 | .0792 | 24.03 | 6.83 |

| SUBSTANCE | 9 $L_T - E_{1T}$ per Cromp-ton. | 10 $L_T - E_{1T}$ per equation 35 | 11 Translational energy | 12 $\frac{\mu}{c}$ from equa'on 38 | 13 $\frac{\mu}{c'}$ from equa'on 39 | 14 Ratio. |
|---|---|---|---|---|---|---|
| Water, $H_2O$ | 197.8 | 194.05 | 104.4 | 1466.6 | 123.22 | 11.90 |
| Carbon dioxide, $CO_2$ | 23.73 | 24.43 | 20.46 | 334.46 | 31.97 | 10.5 |
| Nitrous oxide, $N_2O$ | 22.60 | 21.77 | 20.75 | 321.86 | 33.48 | 9.6 |
| Ethyl alcohol, $C_2H_5OH$ | 45.00 | 60.82 | 32.93 | 880.34 | 60.41 | 14.7 |
| Sulphur dioxide, $SO_2$ | 23.77 | 22.87 | 19.85 | 334.30 | 33.85 | 9.9 |
| Ethyl ether, $(C_2H_5)_2O$ | 21.79 | 22.55 | 18.67 | 449.87 | 42.50 | 10.6 |
| Carbon disulphide, $CS_2$ | 20.31 | 17.34 | 21.31 | 349.35 | 42.88 | 8.1 |
| Benzene, $C_6H_6$ | 28.93 | 28.50 | 21.37 | 463.53 | 43.75 | 10.6 |
| Acetic acid, $C_2H_4O_2$ | 52.48 | 27.68 | 29.30 | 329.46 | 52.61 | 6.3 |
| Ethyl formate, $C_3H_6O_2$ | 24.96 | 26.42 | 20.28 | 466.26 | 42.48 | 11.0 |
| Methyl acetate, $C_3H_6O_2$ | 23.78 | 26.24 | 20.29 | 477.36 | 42.33 | 11.3 |
| Ethyl acetate, $C_4H_8O_2$ | 21.28 | 22.99 | 17.53 | 441.56 | 39.58 | 11.2 |
| Methyl propionate, $C_4H_8O_2$ | 22.77 | 22.70 | 17.92 | 422.97 | 40.44 | 40.4 |
| Propyl formate, $C_4H_8O_2$ | 21.94 | 22.71 | 18.01 | 433.00 | 40.43 | 10.7 |
| Ethylidene chloride, $C_2H_4Cl_2$ | 18.73 | 17.52 | 15.78 | 316.43 | 33.12 | 9.5 |
| Ethyl propionate, $C_5H_{10}O_2$ | 19.87 | 20.82 | 15.96 | 419.16 | 38.45 | 10.9 |
| Isobutyl formate, $C_5H_{10}O_2$ | 18.17 | 19.78 | 15.96 | 422.25 | 38.37 | 11.0 |
| Methyl butyrate, $C_5H_{10}O_2$ | 19.48 | 20.61 | 15.98 | 418.23 | 38.25 | 10.9 |
| Propyl acetate, $C_5H_{10}O_2$ | 19.82 | 21.01 | 15.87 | 420.51 | 38.05 | 11.0 |
| Ethyl butyrate, $C_5H_{10}O_2$ | 18.25 | 19.51 | 14.58 | 413.32 | 37.06 | 11.1 |
| Ethyl isobutyrate, $C_6H_{12}O_2$ | 17.54 | 18.66 | 14.23 | 399.66 | 36.22 | 11.0 |
| Isobutyl acetate, $C_6H_{12}O_2$ | 17.62 | 18.90 | 14.42 | 404.95 | 36.49 | 11.1 |
| Methyl valerate, $C_6H_{12}O$ | 17.20 | 18.52 | 14.31 | 402.57 | 36.31 | 11.1 |

results vary according to the data chosen and the average is given. This variation is only slight as will be seen from Table 8, column 3, where the unaveraged results are given, a result which necessarily follows from the agreement previously shown, equation 27 etc.

The agreeement of the two sets of values is very satisfactory. Out of a total or twenty-three comparisons only six

TABLE 8.

| 1 SUBSTANCE | 2 Temperature C. | 3 $L_T - E$, | 4 $\frac{\mu}{c}$ | 5 Ratio. |
|---|---|---|---|---|
| Water, $H_2O$ | 0 | 199.6 | 1508.8 | 12.24 |
| | 100 | 190.16 | 1437.2 | 11.66 |
| | 200 | 192.38 | 1453.9 | 11.80 |
| Carbon dioxide, $CO_2$ | —25 | 24.84 | 340.10 | 10.64 |
| | 0 | 24.82 | 339.78 | 10.62 |
| | 22.04 | 23.63 | 323.49 | 10.12 |
| Nitrous oxide, $N_2O$ | —20 | 20.25 | 299.29 | 8.94 |
| | 0 | 22.24 | 328.75 | 9.82 |
| | 20 | 22.83 | 337.56 | 10.08 |
| Ethyl alcohol, $C_2H_5OH$ | 0 | 61.75 | 898.75 | 14.80 |
| | 78.2 | 59.90 | 866.93 | 14.34 |
| Sulphur dioxide, $SO_2$ | 0 | 23.62 | 345.17 | 10.19 |
| | 30 | 22.83 | 333.72 | 9.86 |
| | 65 | 22.17 | 324.03 | 9.57 |
| Ethyl ether, $(C_2H_5)_2O$ | 0 | 22.42 | 447.19 | 10.53 |
| | 34.9 | 22.69 | 452.55 | 10.64 |
| Carbon disulphide, $CS_2$ | 0 | 17.24 | 347.32 | 8.10 |
| | 46.2 | 17.44 | 351.39 | 8.19 |
| Benzene, $C_6H_6$ | 0 | 29.20 | 474.91 | 10.86 |
| | 80.4 | 27.80 | 452.14 | 10.34 |

lack agreement by more than two cals and three of these six are within three cals of agreement. $H_2O$, $C_2H_5OH$ and $C_2H_4O_2$ show the worst agreement and all of them have associated molecules at ordinary temperatures. Of these the values for water really furnish a striking confirmation of the formula for the proportional error is small. Alcohol and acetic acid alone fail entirely of agreement.

*The agreement obtained would tend to confirm the law of attraction assumed and also shows that the attraction for many substances remains constant with a change of temperature.*

By still another argument we can confirm the truth of the original formala 26 and the suppositions on which it is based. Using equation 26 and solving for $\mu$ we have for one gram of substance,

$$38. \quad \mu = \frac{(L_t - E_{,t})m^{\frac{1}{3}}c}{d_t^{\frac{1}{3}} - E_t^{\frac{1}{3}}}.$$

In a gas indefinite expansion takes place as the pressure is decreased. This shows that the attraction between the molecules cannot be great enough to make the paths of the molecules closed curves, In a liquid, while undoubtedly many molecules whose velocity is above the average molecular velocity are continually flying away from the surface, yet it must certainly be the case that most of the molecules are drawn back by the molecular attraction. There must be for each substance a certain temperature at which the molecular attraction, without outside pressure, is just strong enough to overbalance the kinetic energy of the average particle and cause it to return to the liquid or solid substance. At this point if the attraction varies as the square of the distance between the molecules we will have $v'^2 = \frac{2\mu}{R}$ where $v'$ is the molecular velocity and is equal to $\left(\frac{3RcT}{m}\right)^{\frac{1}{2}}$ and $R$ is the distance apart of the molecules and is equal to $c\left(\frac{m}{d}\right)^{\frac{1}{3}}$. Hence,

$$39. \quad \mu = c' \frac{T}{m}\left(\frac{m}{d_T}\right)^{\frac{1}{3}}.$$

It is a common text-book expression that at the critical

temperature the kinetic energy of the molecules just balances the attraction and the idea rests on a sound basis, because if the pressure is released expansion takes place at the expense of the molecular energy without the addition of heat as a prerequisite to the expansion. It must be at this point then that equation 39 holds good. On this assumption $\frac{\mu}{c'}$ is calculated, equation 39, and the results are shown in column 13 of Table 7. $\frac{\mu}{c}$ is also calculated equation 38 and the results are given in column 12. Again where data was available at different temperatures only the average is shown in Table 7 and each calculation is given in Table 8, column 4.

Comparing the two equations we have,

$$\frac{(L_t - E_{,t})m^{\frac{1}{3}}}{d_t^{\frac{1}{3}} - D_t^{\frac{1}{3}}} \div \left\{ \frac{T}{m} \left( \frac{m}{d_T} \right)^{\frac{1}{3}} \right\} = \frac{c\mu}{c'\mu}, \text{ or}$$

40. $$\frac{(L_t - E_{,t})\, d_T^{\frac{1}{3}} m}{(d_t^{\frac{1}{3}} - D_t^{\frac{1}{3}})\, T} = \text{constant, where } T \text{ is the critical}$$

temperature. This ratio is shown in Table 7, column 14, average results being given where $t$ could represent more than one temperature and the detailed results are shown in Table 8, column 5. The values obtained seem to approximate 11.0. Out of twenty-three substances examined five, $N_2O$, $C_2H_5OH$, $CS_2$, $C_2H_4O_2$ and $C_2H_4Cl_2$, differ from the average constant by more than ten per cent and of these $C_2H_5OH$, $C_2H_4O_2$, $CS_2$, and $N_2O$, to a less extent have continually failed to agree with the theory and the molecules of $C_2H_5OH$ and $C_2H_4O_2$ are known to be associated at ordinary temperatures.

We must examine a little further the supposition that at the critical temperature the molecular attraction just balances the kinetic energy of the molecule. For if this be true then

the kinetic energy of the molecule as calculated by equation 14. $E_4 = 2.9576 \frac{T}{m}$, divided by 1.007, for the critical temperature should equal the attractive energy calculated from Crompton's formula Table 7, column 9 and from formula 35, column 10. The kinetic energy thus calculated is shown in column 11. The agreement is not usually good, the kinetic energy being almost invariably several (2–6) cals. too small and failing entirely to agree in the case of $H_2O$ and $C_2H_5OH$. The lack of agreement may be due partially to the measurements of the critical density which I have used, or to some influence exerted by the pressure or to one of several other causes, but all my attempts to satisfactorily explain the divergence have so far proved futile. The values columns 9, 10 and 11 are of the same order of magnitude and the disagreement shows some signs of regularity. Therefore I do not think that the lack of agreement necessarily will be found to offer a serious obstacle to what has preceeded.

If the methods outlined in this paper hold true and if the discrepancies can be explained or brought into accord with the theory many lines of investigation are opened. The calculations involved, even with the help of tables, are time consuming and laborious and the necessary data is scattered and somewhat uncertain. Work has been undertaken along several lines but the results are not yet understood or completed sufficiently to justify their publication. Attention will here be called only to one or two attempts.

If a gas at 0° C. and under a constant pressure of one atmosphere be raised one degree in temperature, the amount of energy required to overcome the molecular attraction in producing the expansion which will take place can be easily found from the principles discussed above. Assuming the truth of Gay Lussac's law the energy so required will be,

41. $E_3 = .0000433 \frac{\mu}{c}$, for the expansion of one gram of

gas from 0° to 1° C., where $\frac{\mu}{c}$ has the value calculated from equation 38 and shown in Table 7, column 12. This means that for the given expansion most gases will require about .01 to .02 cals. to overcome the molecular attraction alone. All evidence goes to show that the amount of energy so required is *as a matter of fact by no means so large.* Nor does the law of attraction assumed lead to the equation given by Van der Waals.

Equations 38 and 39 afford a method of determining the relative attraction between molecules and hence permit of a further study of the law of attraction. This attraction appears to depend primarily upon the chemical nature of the molecule and not upon its mass. We may say therefore that *the molecular attraction appears to resemble the attraction of gravitation in that it varies inversely as the square of the distance apart of the attracting molecules and does not vary with the temperature.* It differs from the attraction of gravity in being determined primarily by the construction of the molecule and not by its mass.

Again if the argument pursued is strictly true the increase of the specific heat of a liquid over the specific heat of a gas at constant volume must be spent primarily in increasing the distance apart of the molecules and in changing the vapor pressure of the liquid, but no general quantitative relations have here been reached.

The work has also a bearing upon boiling points, vapor pressure, and Trouton's formula. Efforts to establish some quantitative relations along these lines have not entirely failed but point strongly to the belief that the work can be extended to important conclusions in the directions indicated.

Here also the work of A. Behn[258] must be noticed. He found for a number of metals and alloys, also graphite, that the specific heat of the solid decreased as the temperature was lowered according to a parabolic law, his observation extending to —186° C. As the preceeding discussion of the latent

heat of vaporization is based on the assamption that the total "internal" heat energy of a molecule of a liquid was proportional to the translational energy of the molecule and hence to the temperature the conclusion was drawn that the specific heat of the liquid multiplied by the absolute temperature of the melting point must be three times the latent heat of fusion. For a parabola is two thirds of the circumscribing rectangle and thus one third of the energy required to raise the temperature of the substance must be added at the melting point. The conclusion was at once verified for mercury and later, while searching for data to extend the conclusion it was found that J. W. Richards[254] had in 1893 empirically discovered and published the law as true for many metals. If the possible causal connection between Richard's formula and Behn's work has been noticed heretofore it has escaped my attention.

In conclusion I wish to acknowledge and here express my thanks for the encouragement, criticism, and helpful suggestion given me during the progress of this work by Dr. Chas. Baskerville.

## SUMMARY.

1. The forces existent between molecules of gases under ordinary conditions must be very slight as shown by a study of $\sigma_p$ and $\gamma$.

2. Particular attention is called to the equation, $\sigma_p\left(\frac{\gamma-1}{\gamma}\right)$ = constant. It is shown to be capable of a physical interpretation if applied to solid and liquid molecules and its relation to the law of Dulong and Petit is suggested.

3. Evidence is brought forward to show that molecules do not rotate as more or less rigid bodies.

4. An effort is made to explain the unusually high atomic heat energy of some compounds.

5. Evidence is advanced to prove that:—

a. Molecular attraction varies inversely as the square of the distance apart of the molecules.

b. The absolute molecular attraction is only slighly affected by changes in temperature.

c. The molecular attraction depends primarily upon the chemical constitution of the molecule and not upon its mass.

6. A connection between the parabolic decrease of the specific heat of some metals and the formula of Richards (specific heat of liquid $\times$ absolute temperature of melting point $\div 3 =$ latent heat of fusion) is shown.

J. E. Mills.

# AUTHORITIES.

The following works are referred to by number in the citations of authority. No effort is made to give the original source of the data but tables are freely used, especially "Landolt and Börnstein."


1. Physikalisch-Chemische Tabellen".—Landolt and Börnstein.
2. Smithsonian Physical Tables, 1897.
3. A Table of Specific Gravity for Solids and Liquids.—F. W. Clarke.
4. Heat for Advanced Students.—Edwin Edser.
5. Argon: a New Constituent of the Atmosphere.—Lord Rayleigh and Prof. Wm. Ramsay.
6. Ratio of Specific Heats.—O. Lummer and E. Pringshein.
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15. Encylopaedia Brittanica.
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20. Introduction to Physical Chemistry.—Walker.
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23. Philosophical Transactions.

# CITATIONS.

1. 23, vol 182a, p 73, and vol 185a, p 943.
2. 7 p 35.
3. Average of $.0_4 89873$ Morley (10 p 110) and the value at Paris given by Rayleigh $.0_4 8991$ (12 vol 53 no. 322 p 147) reduced to Lat. 45° by division by the factor 1.000333 (1 p 8). The value given by Rayleigh was deduced from the values,
   $.0_4 8958$, Regnault.
   $.0_4 8988$, Regnault, corrected by Crafts.
   $.0_4 8985$, Leduc.
   $.0_4 9001$, Rayleigh, leaving out the uncorrected value of Regnault.
4. Mercury at 0° referred to water at 4°. Average of 13.5956, Marek (2 p 95).
   13.5958–13.5960, Regnault (1 p 119).
   13.5952–13.5954, Volkman (1 p 119).
5. 1 p 6.
6. 14, vol 6, no. 33, p 193.
7. 3.3996, at —28° to 9°, 1 p 339, Regnault.
   3.410, " 21° " 100°, " Wiedemann.
   3.409, " 12° " 198°, " Regnault.
8. .2425, " 23° " 99°, " Wiedemann.
   .2426, " 26° " 198°, " Wiedemann.
9. .2438, " 0° " 200°, " Regnault.
10. .21751, " 13° " 207°, " Regnault.
11. .18427, " 28° " 7°, " Regnault.
    .20246, " 15° " 100°, " Regnault.
    .21692, " 11° " 214°, " Regnault.
12. .22616, " 16° " 207°, " Regnault.
    .2126, " 26° " 103°, " Wiedemann.
    .2241, " 27° " 206°, " Wiedemann.
13. .15439, " 16° " 202°, " Regnault.

14. 1.410, Cazin, 5 p 36.
1.3852, Röntgen, 6 p 29.
1.407, Dulong, 5 p 36.
1.394, Dulong, corrected by Wüllner, 16 p 125.
1.401, Masson, 5 p 36.
1.405, Masson, corrected by Wüllner, 16 p 125.
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1.410, Jamin and Richard, 5 p 36.
1.4084. Lummer and Pringsheim, 6 p 29.
1.384, Manoevrier, 6 p 29.
1.391, Rayleigh and Ramsay, 5 p 36.
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15. 1.4032, Wüllner, 1 p 340.
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1.410, Dulong, corrected by Wüllner, 16 p 125.
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18. 1.291, Cazin, 1 p 340.
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1.2653, Muller, 1 p 340.
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1.2995, Lummer and Pringsheim, 6 p 29.
1.298, Manoevrier, 6 p 29.
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1.308, Capstick, 16 p 125.

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1.2724, at 100°, Wüllner, 1 p 140.
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20. 1.262, Cazin, 1 p 340.
1.2562, Muller, 1 p 340.
1.248, Masson, 16 p 126,

21. .0036613, 0° to 100°, Regnault, 1 p 110.

22. .0036668, 0° to 100°, Regnault, 1 p 110.

23. .003673, calculated from Joule-Thomson effect, 15 art. heat.

24. .003674, calculated from Joule-Thomson effect, 15 art. heat.

25. .0037099, 0° to 100°, Regnault, 1 p 110.
.003629, at 6°, Andrews, calculated to 0° = .0037098, 1 p 110.

26. .0037195, 1° to 100°, Regnault, 1 p 110.

27. .0039028, 0° to 100°, Regnault, 1 p 110.
.00413, 0° to 10°, at 10° Amagat, reduced to 0° = .004308, 1 p 110.

28. Density of air = 1.29347 at Paris, Rayleigh. Reduced [3] to Lat. 45° = 1.29304 (12 vol 53, no. 322 p 147).

29. .96779 $Air^{28} = 1$, Wrede, 1 p 116.

30. 1.2505 at Paris, Rayleigh and Ramsay, 5 p 5.

31. 1.42961 at Paris, Rayleigh, (12 vol 53, no. 322 p 147.) This value was deduced from
1.42980, Regnault.
1.43011, Regnault, corrected by Crafts
1.42939, Von Jolly.
1.42971, Von Jolly, corrected by Rayleigh.
1.42910, Leduc.

1.42952, Rayleigh, omitting uncorrected results. The average reduced[3] to Lat. 45° gives 1.429134 which was averaged with 1.42900, Morley, 10 p 110.

32. 1.52901 $Air^{28} = 1$, Regnault, 1 p 116.
33. 1.614 $Air^{28} = 1$, Dalton, 1 p 116.
34. 2.277 $Air^{28} = 1$, Buff, 1 p 116.
35. 15 Art. Heat.
36. 11 vol, 23 p 94.
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37. .59295, at 18° to 208°, Regnault, 1 p 339.
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.5356, " 27° " 200°, Wiedemann, 1 p 339.
.51246, " 24° " 216°, Regnault, 1 p 339.
39. .3787, " 100° to 125°, Gray, 1 p 339.
.48051, " 128° " 217°, Regnault, 1 p 339.
40. .23173, " 13° " 172°, Regnault, 1 p 339.
41. .24514, " 20° " 206°, Regnault, 1 p 339.
42. .1940, " 13° " 100°, Strecker, 1 p 339.
.1867, " 22° " 214°, Regnault, 1 p 339.
43. .45341, " 108° " 220°, Regnault. 1 p 339.
44. .1241, " 13° " 202°, Regnault, 1 p 339.
.1155, " 16° " 343°, Strecker, 1 p 339.
45. .4280, " 25° " 111°, Wiedemann, 1 p 339.
.4618, " 27° " 189°, Wiedemann, 1 p 339.
.47966, " 79° " 224°, Regnault, 1 p 339.
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47. .0820, " 11° " 100°, Strecker, 1 p 339.
48. .22931, " 111° " 221°, Regnault, 1 p 339.
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.0553, " 19° " 338°, Strecker, 1 p 339.
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54. .0336, " 206° " 377°, Strecker, 1 p 339.
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1.3172, at 0°, Wüllner, 1 p 339.
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57. 1.277, at 103° to 104°, de Lucchi, 1 p 340.
1.274, at 78°, Beyme, 1 p 340.
1.287, at 144° to 300°, Cohen, 1 p 340.
58. 1.394, at 10° to 40°, Masson, corrected by Wüllner, 16 p 125.
59. 1.2759, Muller, 1 p 340.
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1.389, at 20°, Strecker, 1 p 340.
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70. 1.315, at 100°, Strecker, 1 p 340.
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115. 19 vol 17, no. 235, 1901 p 61.
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.8142, Kopp, 3 p 188.
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169. .7476, at 61.8°, Schiff, 3 p 188.
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170. .7135, Ramsay and Young, 3 p 188.

171. 263.86, Favre and Silbermann, 1 p 348.
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175. The densities and latent heats are often determined only near the boiling point—or they are determined at the boiling point and a wrong boiling point given. In such cases I have usually averaged the boiling point determinations with the temperatures used for the other observations. An error is thus introduced, but it is not large, and I deemed this the most accurate method of averaging.

176. 1.630, Pierre, 3 p 291.
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177. 1.466, Ramsay, 3 p 291.
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181. See note 175. Schiff 46.5°, Thorpe 46.04°, Buff 46°, 3 p 57 and 1 p 188.

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195. .6956, Ramsay, 3 p 197.
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.8957, Warren, 3 p 169.
.8995, Longuinine, 3 p 169.
.90023, Adrienz, 3 p 169.
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.8126, at 80°, Louguinine, 3 p 169.
.8133, at 80°, Adrienz, 3 p 169.
.8142, at 80°, Ramsay, 3 p 169.
.8111, at 80°, Schiff, 3 p 169.
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203. 93.45, Schiff, 1 p 348.
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204. 1 p 331 and 2 p 222.
205. 19 Vol. 17, No. 235, (10–4 1901) p 61.
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208. See note 175. 53.4°, Schiff, 24.4°; Elsässer; 54.3°, Andrews; 3 p 205, 1 p 348.
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74.6°, Andrews, 1 p 349.
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213. .8309, at 73.74°, Naccari and Pagliani, 3 p 207.
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215. .84225, at 78.5°, Schiff, 3 p209.
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217. .8215, Elsässer, 3 p 206.
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218. Note 175. 56° Ramsay; 59.9° Thorpe; 56.6 Schiff, 57.8°; 9, Beilage 1897 p 95, 3 p 296.

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235. .77080, at 116.3°, Elsässer, 3 p 208.
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235. Schiff, 1 p 349. See note 175.

236. .7767, at 127.3°, Gartenmeister, 3 p 212.

237. 84.9, at 118°, Ogier, 1 p 349.

238. 105.30, at 54.3°, Andrews, 1 p 348.
100.4, Berthelot and Ogier, 1 p 348.
92.15, at 53.5°, Schiff, 1 p 348.

239. 110.2, at 55°, Andrews, 1 p 349.
93.95, at 57.3°, Schiff, 1 p 349.

240. 92.68, at 74.6°, Andrews, 1 p 349.
83.07, at 77°, Schiff, 1 p 349.
84.28, at 73.1°, Wirtz, 1 p 349.

241. 84.15, at 80°, Schiff, 1 p 349.

242. 85.25, at 81.2°, Schiff, 1 p 349.

243. 67.02, Berthelot and Ogier, 1 p 348.

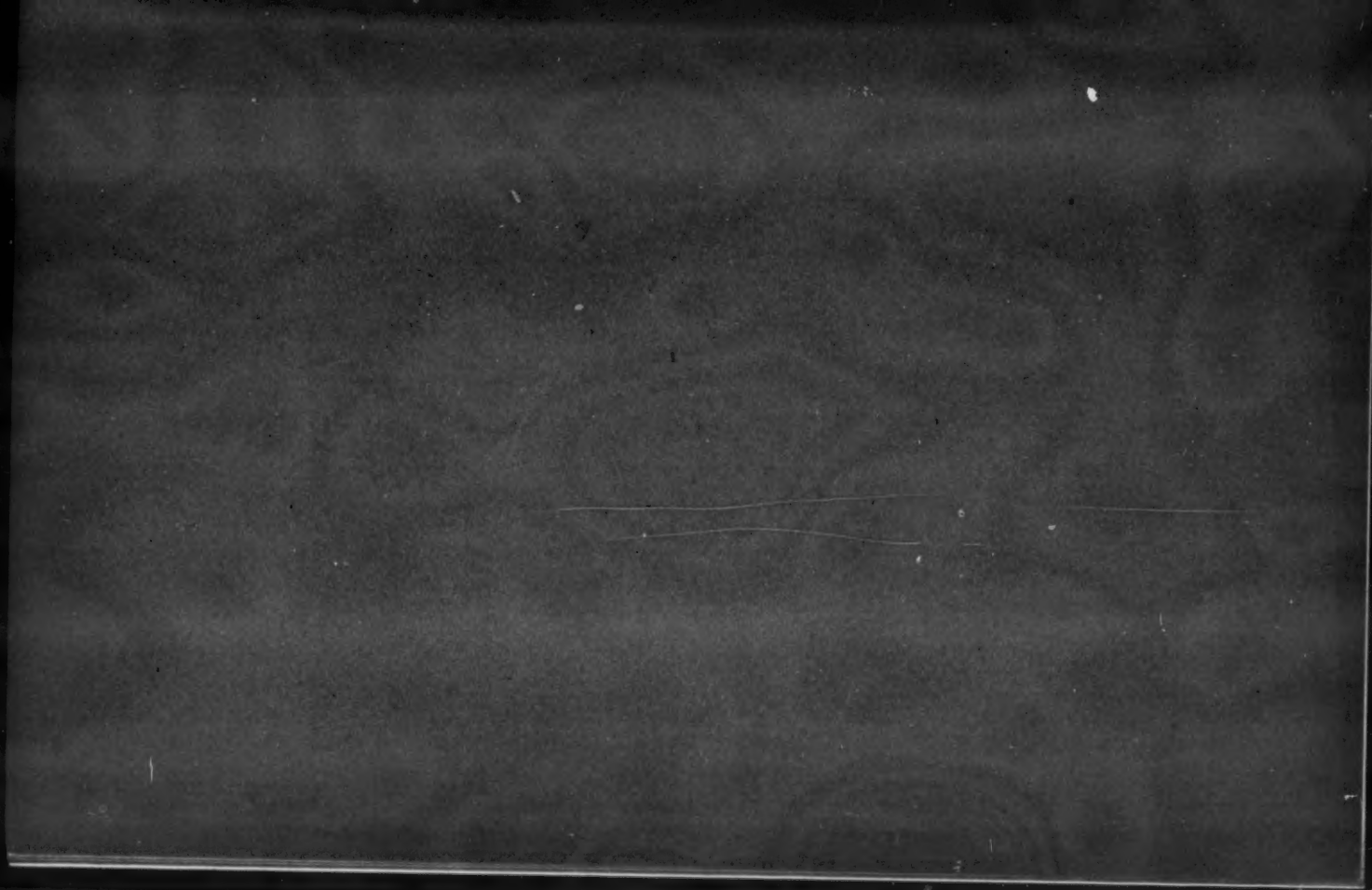
244. 77.1, at 98.7°, Schiff, 1 p 349.

245. 77.25, at 102.3°, Schiff, 1 p 349.

246. 77.3, at 102.3°, Schiff, 1 p 349.

247. 71.5, at 119°, Schiff, 1 p 349.

248. 69.2, at 110°, Schiff, 1 p 349.

249. 69.9, at 116.8°, Schiff, 1 p 349.

250. 69.95, at 116.3°, Schiff, 1 p 349.
251. 20 p 206.
252. The critical data given are taken from 1 p 84 by averaging the *observations.*
253. 21, 1—257—1900.
254. 22, July, Aug. and Sept. 1893.